

OHIO STATE UNIVERSITY
4th INTERNATIONAL SYMPOSIUM ON
MOLECULAR SPECTROSCOPY
JUNE 13-17, 1994



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The U.S. Army Research Office
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Department of Chemistry
Department of Physics

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OHIO STATE UNIVERSITY INTERNATIONAL SYMPOSIUM ON MOLECULAR SPECTROSCOPY 4th JUNE 13-17, 1994

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Please send correspondence to:

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* steering committee member

BANQUET

The Banquet will take place at the Ohio State University Faculty Club (H) on Wednesday, June 15, 1994. A reception with cash bar will be held at 6:00 p.m. with the Banquet following at 7:00 p.m. Dr. Boris Stoicheff, Department of Physics, University of Toronto, will speak on "TREASURES OF BYGONE COLUMBUS SYMPOSIA." A very limited number of tickets will be available the first day of the Symposium.

SCHEDULING

Please check your abstract book closely. Since the preliminary program was printed, a number of post-deadline talks have been added (many, but not all, in the Friday sessions) and a small number of schedule changes were necessary. All changes and additions have been marked in the program. Any modifications since the printing of this book are given on a separate sheet in your packet.

EXHIBITORS

We are again pleased to have a number of technical exhibitors and publishers represented at the Symposium. We wish especially to thank Coherent, Inc. for supporting the coffee and doughnuts. Their exhibit is located in the coffee room. The complete list of exhibitors and their location is provided on a separate page in your packet. Please try to stop by and visit the exhibits.

50th SYMPOSIUM

Please mark your calendars and plan to attend the 50th Ohio State University International Symposium on Molecular Spectroscopy, June 12-16, 1995. Plans are already underway for a suitable celebration of the Golden Anniversary of the Symposium.

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
<small>Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.</small>				
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6. AUTHOR(S) Terry A. Miller				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Ohio State University Department of Chemistry 120 W. 18th Ave Columbus OH 43210			8. PERFORMING ORGANIZATION REPORT NUMBER	
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12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited.			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) The Ohio State University International Symposium on Molecular Spectroscopy is one of the longest running and most successful scientific conferences in the United States today. It plays a unique role in the educational development of large numbers of graduate students in the physical sciences. The Conference's subject area underlies many items of direct interest to ARO, such as interactions of electro-magnetic radiation with molecules, characterization and quantification of low-level molecular concentrations, such as contaminants, pollutants, reactive intermediates in combustion, etc.				
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MONDAY, JUNE 13, 1994--8:45A.M.

AUDITORIUM HITCHCOCK HALL

Chair: FRANK DELUCIA, The Ohio State University, Columbus, Ohio

Welcome

Edward F. Hayes, Vice President for Research
The Ohio State University

MA01 NEW INTERSTELLAR MOLECULES

40 min

P. THADDEUS, Division of Applied Sciences and Center for Astrophysics, Harvard University, Cambridge MA 02138.

MA02 LARGE AMPLITUDE MOTIONS OF MOLECULES AND IONS REVEALED BY
SUPERSONIC JET SPECTROSCOPY

40 min

MITSUO ITO, Institute for Molecular Science, Okazaki National Research Institutes, Myodaiji, Okazaki 444, Japan.

INTERMISSION

PRESENTATION OF 1993 RAO PRIZE AWARDS

Jennifer M. Campbell, University of Waterloo
Hao Li, Cornell University
J. Bradley White, University of Waterloo

MA03 *COBLENTZ PRIZE AND AWARD LECTURE*
ELECTRONIC SPECTRA OF SEMICONDUCTOR NANOCRYSTALS

40 min

A. PAUL ALIVISATOS, Department of Chemistry, University of California, Berkeley, Ca 94720.

Accession For	
NTIS	<input checked="" type="checkbox"/>
CRA&I	<input checked="" type="checkbox"/>
DTIC	<input type="checkbox"/>
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Justification _____	
By _____	
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Availability Codes	
Dist	Avail and/or Special
A-1	

MONDAY, JUNE 13, 1994--1:30P.M.

ROOM 1153 SMITH LAB

Chair: LAURENCE S. ROTHMAN, AF Geophysics Directorate, Hanscom AFB, Massachusetts

ME01 THE COLLISION-INDUCED FUNDAMENTAL BAND OF NITROGEN AT LOW TEMPERATURES 15 min 1:30

W. B. OLSON, 348 North Summit Ave., Gaithersburg, MD 20877; W. J. LAFFERTY, A. WEBER, Molecular Physics Division, NIST, Gaithersburg, MD 20899; and A. M. SOLODOV, Institute of Atmospheric Optics, 1 Academicheskij Ave., 634055 Tomsk, Russia.

ME02 THE OVERTONE TRANSITIONS OF $^{12}\text{C}^{16}\text{O}_2$ AND $^{13}\text{C}^{16}\text{O}_2$ IN THE NEAR INFRARED 15 min 1:47

X. YANG and C. NODA, Department of Chemistry, University of New Hampshire, Durham, NH 03824.

ME03 PRESSURE BROADENING AND SPIN SPLITTINGS IN THE ν_3 -BAND OF NO_2 15 min 2:04

B. SUMPE, V. V. PUSTOGOV, P. HEINTGES, Optisches Institut der Technischen Universität Berlin, Sekr. PN 0-1 Hardenbergstraße 36, 10623 Berlin, Germany; F. KÜHNEMANN, University of Chicago, Department of Chemistry, 5735 S. Ellis Avenue, Chicago, IL 60637; and H. -D. KRONFELDT, Optisches Institut der Technischen Universität Berlin, Sekr. PN 0-1 Hardenbergstraße 36, 10623 Berlin, Germany.

ME04 H_2O LINE POSITION MEASUREMENTS AT 1000K 15 min 2:21

M. P. ESPLIN, R. B. WATTSON, Stewart Radiance Laboratory, Utah State University, 139 The Great Road, Bedford, MA 01730; and M. L. HOKE, Geophysics Directorate, Phillips Laboratory/GPOS, 29 Randolph Road, Hanscom AFB, Bedford, MA 01731.

ME05 CHARACTERIZATION OF CANDIDATE DIAL LIDAR WATER VAPOR ABSORPTION LINES IN THE TWO MICRON REGION 10 min 2:38

MICHAEL E. THOMAS, RAYMOND M. SOVA, The Johns Hopkins University, Applied Physics Laboratory, Laurel, Maryland 20723; DAVID TOBIN, DANIEL BYRUM and L. LARRABEE STROW, Department of Physics, University of Maryland Baltimore County, Baltimore Maryland 21228.

ME06 SHIFTS OF H_2O SPECTRAL LINES IN THE $\nu_1 + 3\nu_3$ VIBRATIONAL BAND INDUCED BY THE PRESSURE OF NOBLE GASES 15 min 2:50

A. D. BYKOV, V. V. LAZAREV, Yu. N. PONOMAREV, V. N. STROINOVA and B. A. TIKHOMIROV, Institute of Atmospheric Optics, SB Russian Sci. Acad., Tomsk, 634055, Russia.

INTERMISSION

- | | | | |
|------|---|--------|------|
| ME07 | TEMPERATURE DEPENDENCE OF AIR-BROADENING AND SHIFT COEFFICIENTS OF O_3 LINES IN THE ν_1 BAND | 10 min | 3:30 |
| | <p><u>M. A. H. SMITH</u>, NASA Langley Research Center, Atmospheric Sciences Division, Mail Stop 401A, Hampton Virginia 23681-0001; <u>V. MALATHY DEVI</u>, <u>D. CHRIS BENNER</u>, Department of Physics, The College of William and Mary, Williamsburg, VA 23187-8795; and <u>C. P. RINSLAND</u>, NASA Langley Research Center, Atmospheric Sciences Division, Mail Stop 401A, Hampton Virginia 23681-0001.</p> | | |
| ME08 | TEMPERATURE DEPENDENCE OF AIR-BROADENING AND SHIFT COEFFICIENTS OF $^{16}O_3$ LINES IN THE ν_2 BAND | 10 min | 3:42 |
| | <p><u>V. MALATHY DEVI</u>, <u>D. CHRIS BENNER</u>, Department of Physics, The College of William and Mary, Williamsburg, VA 23187-8795; <u>M. A. H. SMITH</u> and <u>C. P. RINSLAND</u>, NASA Langley Research Center, Atmospheric Sciences Division, Mail Stop 401A, Hampton Virginia 23681-0001.</p> | | |
| ME09 | PRESSURE BROADENING IN THE ν_1 BAND OF SO_2 : COLLISIONS WITH SO_2 , N_2 , AIR, He, Ne, Kr, Ar, Xe | 15 min | 3:54 |
| | <p><u>B. SUMPF</u>, <u>O. FLEISCHMANN</u>, <u>Y. HEINER</u>, <u>J. WASCHULL</u>, <u>I. MEUSEL</u>, and <u>H. -D. KRONFELDT</u>, Optisches Institut der Technischen Universität Berlin, Sekr. PN 0-1 Hardenbergstraße 36, 10623 Berlin, Germany.</p> | | |
| ME10 | LINESHAPE ASYMMETRIES IN Ar-BROADENED $HF(v=1-0)$ IN THE DICKE-NARROWING REGIME | 15 min | 4:11 |
| | <p><u>A. S. PINE</u>, Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, MD 20899.</p> | | |
| ME11 | AN EMPIRICAL EXPRESSION FOR LINE WIDTHS OF AMMONIA FROM FAR-INFRARED MEASUREMENTS | 15 min | 4:28 |
| | <p><u>L. R. BROWN</u>, ms 183-301, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109; and <u>D. B. PETERSON</u>, ms 183-601, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109.</p> | | |
| ME12 | LINE MIXING IN THE ν_3 BAND OF METHANE | 15 min | 4:45 |
| | <p><u>D. CHRIS BENNER</u>, <u>V. MALATHY DEVI</u>, Department of Physics, College of William and Mary, Williamsburg, VA 23187-8795; <u>MARY ANN H. SMITH</u> and <u>CURTIS P. RINSLAND</u>, Atmospheric Sciences Division, NASA Langley Research center, Hampton, VA 23681-0001.</p> | | |
| ME13 | PRESSURE BROADENING OF LARGER MOLECULES - THE ν_{14} -BAND OF C_6H_6 | 15 min | 5:02 |
| | <p><u>B. SUMPF</u>, <u>J. WASCHULL</u>, <u>Y. HEINER</u>, <u>I. MEUSEL</u>, <u>F. KÜHNEMANN</u>, <u>V. V. PUSTOGOV</u>, and <u>H. -D. KRONFELDT</u>, Optisches Institut der Technischen Universität Berlin, Sekr. PN 0-1 Hardenbergstraße 36, 10623 Berlin, Germany.</p> | | |

ME14 CALCULATION OF ROTATIONAL STATE-TO-STATE OZONE RELAXATION RATES 10 min 5:19
FOR O_3-N_2 , O_3-O_2 AND O_3-O_3 COLLISIONS AND MODELIZATION OF THE $(100) \rightleftharpoons (001)$
CORIOLIS-ASSISTED INTERMODE TRANSFER

F. MENARD-BOURCIN, C. BOURSIER, C. BOULET, L. DOYENNETTE, J.
MENARD and J. -M. FLAUD, Laboratoire de Physique Moléculaire et Applications,
CNRS, Université P. et M. Curie, Tour 13, Bte 76, 4 Place Jussieu, 75252 Paris
Cedex 05, France.

MONDAY, JUNE 13, 1994--1:30P.M.

ROOM 1009 SMITH LAB

Chair: C. WELDON MATHEWS, The Ohio State University, Columbus, Ohio

- MF01 EXTENSION OF THE ABSORPTION PATH LENGTH IN A CRYOGENIC SAMPLE: THE INFRARED SPECTRUM OF SOLID H₂ MEASURED WITH PATH LENGTHS OF 3.8, 15, AND 33 CM 15 min 1:30

R. A. STEINHOFF, B. P. WINNEWISSER, M. WINNEWISSER, Physikalisch-Chemisches Institut, Justus-Liebig-Universität Giessen, Heinrich-Buff-Ring 58, D-35392 Giessen, Germany; and K. NARAHARI RAO, Department of Physics, The Ohio State University, 174 West 18th Avenue, Columbus, Ohio 43210.

- MF02 CONDON MODULATION SPECTROSCOPY OF SOLID HYDROGEN 20 min 1:47

KAREN E. KERR, DAVID P. WELIKY, University of Chicago, Department of Chemistry, 5735 S. Ellis, Chicago, IL 60637-1403; TAKAMASA MOMOSE, Department of Chemistry, Faculty of Science, Kyoto University, Kyoto 606-01, Japan; ROBERT M. DICKSON and TAKESHI OKA, University of Chicago, Department of Chemistry, 5735 S. Ellis, Chicago, IL 60637-1403.

- MF03 EXTENDED OBSERVATION AND COMPREHENSIVE ASSIGNMENT OF THE Q₁(0) VIBRATIONAL SPECTRA OF D₂ AND HD IMPURITIES IN SOLID PARAHYDROGEN 15 min 2:09

DAVID WELIKY, KAREN E. KERR, TERESA J. BYERS, YU ZHANG and TAKESHI OKA, University of Chicago, Department of Chemistry, 5735 S. Ellis, Chicago, IL 60637-1403.

- MF04 OBSERVATION AND ANALYSIS OF THE Q₃(0) TRANSITION OF SOLID PARAHYDROGEN 15 min 2:26

ROBERT M. DICKSON, TAKAMASA MOMOSE, Department of Chemistry, Faculty of Science, Kyoto University, Kyoto 606-01, Japan; TERESA J. BYERS, KAREN E. KERR and TAKESHI OKA, University of Chicago, Department of Chemistry, 5735 S. Ellis, Chicago, IL 60637-1403.

- MF05 OBSERVATION OF THE S₃(0) TRANSITION IN SOLID PARAHYDROGEN AND THE DEVELOPMENT OF A THEORY OF $\Delta J=2$ ROVIBRATIONAL LINEWIDTHS 20 min 2:43

ROBERT M. DICKSON and TAKESHI OKA University of Chicago, Department of Chemistry, 5735 S. Ellis, Chicago, IL 60637-1403.

INTERMISSION

- MF06 MULTIPHONON ABSORPTION IN DIAMOND 15 min 3:20

MICHAEL E. THOMAS, The Johns Hopkins University, Applied Physics Laboratory, Laurel, Maryland 20723.

- | | | | |
|------|--|--------|------|
| MF07 | EXPERIMENTAL AND SIMULATED SPECTRA OF ICE SURFACES, BARE AND WITH ADSORBATES: ASSIGNMENT OF SURFACE-LOCALIZED MODES | 15 min | 3:37 |
| | <u>B. ROWLAND</u> , J. P. DEVLIN and N. S. KADAGATHUR, Department of Chemistry, Oklahoma State University, Stillwater, OK 74078. | | |
| MF08 | PREFERENTIAL DEUTERIUM BONDING AT MICROPORE SURFACES OF AMORPHOUS ICE | 15 min | 3:54 |
| | <u>LANCE DELZEIT</u> and J. P. DEVLIN, Department of Chemistry, Oklahoma State University, Stillwater, OK 74078. | | |
| MF09 | INFRARED SPECTRUM OF CF ₃ H ADSORBED ON ALKALI HALIDE FILMS | 15 min | 4:11 |
| | <u>C. A. BAUMANN</u> , Department of Chemistry, University of Scranton, Scranton, PA 18510. | | |
| MF10 | LASER EXCITED FLUORESCENCE FROM ORGANIC DYES RELEASED FROM LIPOSOMES | 10 min | 4:28 |
| | <u>P. MISRA</u> , Laser Spectroscopy Laboratory, Department of Physics & Astronomy, Howard University, Washington, DC 20059; <u>D. L. VANDERMEULEN</u> , Organics/LaGrange, Inc., 7125 N. Clark Street, Chicago, IL 60073; and <u>K. G. SPEARS</u> , Department of Chemistry, Northwestern University, Evanston, IL 60208. | | |
| MF11 | CONCENTRATIONAL DEPENDENCE OF REVERSIBLE DYNAMIC BLEACHING PROCESSES FOR POROUS SILICATE GLASSES ACTIVATED BY ORGANIC DYE MOLECULES IN STRONG OPTICAL FIELDS | 10 min | 4:40 |
| | <u>V. N. BEGER</u> , Department of Physics, Saint-Petersburg, Institute of Fine Mechanics and Optics, ul. Sablynskaya I4, Saint-Petersburg 197101 Russia. | | |
| MF12 | STUDY OF ATOMS, IONS AND CLUSTERS OF SUPPORTED SILVER BY THE METHOD OF DIFFUSE REFLECTANCE ELECTRON SPECTROSCOPY | 10 min | 4:52 |
| | <u>A. N. PESTRYAKOV</u> , A. N. DEVOCHKIN and A. A. DAVIDOV, Tomsk Institute of Civil Engineering, Russia, Institute of Catalysis, Russia. | | |
| MF13 | EXCITON - INDUCED PROCESSES IN SOLID MOLECULAR OXYGEN - NEON SOLUTIONS | 10 min | 5:04 |
| | <u>A. G. BELOV</u> , I. Ya. FUGOL and E. M. YURTAEVA, B. Verkin Institute for Low Temperature Physics and Engineering, Ukrainian Academy of Sciences, 47 Lenin Avenue, 310164 Kharkov, Ukraine. | | |
| MF14 | FLUORESCENCE STUDY OF DEFECT FORMATION VIA EXCITON TRAPPING INTO MOLECULAR STATES IN RARE GAS SOLIDS | 10 min | 5:16 |
| | <u>E. V. SAVCHENKO</u> , S. A. GUBIN, O. N. GRIGORASHCHENKO and A. N. OGURTSOV, Department of Spectroscopy, B. Verkin Institute for Low Temperature Physics and Engineering, Ukrainian Academy of Sciences, 310164 Kharkov, Ukraine. | | |

MONDAY, JUNE 13, 1994--1:30P.M.

ROOM 1005 SMITH LAB

Chair: BOR-CHEN CHANG, Brookhaven National Laboratories, Upton, New York

MG01	THE MICROWAVE SPECTRUM OF DICHLOROSILYENE SiCl_2 IN EXCITED VIBRATIONAL STATES	15 min	1:30
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MASAHARU FUJITAKE, Department of Physics, Faculty of Science, Kanazawa University, Kanazawa 920, Japan; and EIZI HIROTA, The Graduate University for Advanced Studies, 4259 Nagatsuta, Midori, Yokohama 227, Japan.

MG02	DETECTION AND STRUCTURE OF CARBON-CHAIN SINGLET MOLECULES, C_nO ($n=5,7,9$), BY PDN-FTMW SPECTROSCOPY	15 min	1:47
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TERUHIKO OGATA, Faculty of Liberal Arts, Shizuoka University, Ohya, Shizuoka 422, Japan; YASUHIRO OHSHIMA and YASUKI ENDO, Department of Pure and Applied Sciences, College of Arts and Sciences, The University of Tokyo, Komaba, Meguro-ku, Tokyo 153, Japan.

MG03	DETECTION OF CARBON-CHAIN TRIPLET MOLECULES, C_nO ($n=2,4,6,8$), BY PDN-FTMW SPECTROSCOPY	15 min	2:04
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YASUHIRO OHSHIMA, Department of Pure and Applied Sciences, College of Arts and Sciences, The University of Tokyo, Komaba, Meguro-ku, Tokyo 153, Japan; TERUHIKO OGATA, Faculty of Liberal Arts, Shizuoka University, Ohya, Shizuoka 422, Japan; and YASUKI ENDO, Department of Pure and Applied Sciences, College of Arts and Sciences, The University of Tokyo, Komaba, Meguro-ku, Tokyo 153, Japan.

MG04	VIBRATIONAL AND ROTATIONAL LASER SPECTROSCOPY OF SUPERSONICALLY COOLED ALKOXY AND ALKYLTHIO RADICALS	15 min	2:21
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P. MISRA, X. ZHU, M. M. KAMAL, A. H. NUR, and H. L. BRYANT, JR., Laser Spectroscopy Laboratory, Department of Physics & Astronomy, Howard University, Washington, D.C. 20059.

MG05	VIBRONIC STRUCTURES AND AUTOCORRELATION FUNCTIONS OF GROUND STATE CH_3O , CD_3O , AND $\text{CH}_3\text{CH}_2\text{O}$	15 min	2:38
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A. GEERS, J. KAPPERT, X. LI, C. STÖCK, F. TEMPS and J. WIEBRECHT, MPI für Strömungsforschung, Bunsenstrasse 10, 37073 Göttingen, Germany.

- MG06 ELECTRONIC SPECTROSCOPY OF CF₃O IN A SUPERSONIC JET 15 min 2:55
- MIN-CHIEH YANG, Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, 120 West Avenue, Columbus, Ohio 43210; XUE-QING TAN, University of Michigan, Department of Chemistry, 930 North University, Ann Arbor MI 48109-1055; CHRISTOPHER C. CARTER, JAMES M. WILLIAMSON, TERRY A. MILLER, Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, 120 West Avenue, Columbus, Ohio 43210; TODD E. MLSNA, J. D. O. ANDERSON and DARRYL D. DESMARTEAU, Department of Chemistry, H. L. Hunter Chemistry Laboratory, Clemson University, Clemson, South Carolina 29634.

INTERMISSION

- MG07 MULTIPHOTON IONIZATION DIAGNOSTICS FOR FLUORINATED ETHYL RADICALS: STRUCTURAL CONSIDERATIONS FOR DIFLUOROETHYL RADICALS 15 min 3:30

JEFFREY L. BRUM, RUSSELL D. JOHNSON III and JEFFREY W. HUDGENS, Chemical Kinetics and Thermodynamics Division, National Institute of Standards and Technology, Gaithersburg, MD 20899.

- MG08 DIODE LASER SPECTROSCOPY OF THE JET-COOLED PROPARGYL RADICAL PRODUCED BY THE PHOTOLYSIS OF UV LASER 10 min 3:47

YOSHIHIRO SUMIYOSHI, TAKESHI IMAJO, TAKEHIKO TANAKA and KEIICHI TANAKA, Department of Chemistry, Faculty of Science, Kyushu University 33, Hakozaki, Higashiku, Fukuoka 812, Japan.

- MG09 TIME-RESOLVED DIODE LASER SPECTROSCOPY OF THE ν_6 BAND OF THE PROPARGYL RADICAL 15 min 3:59

KEIICHI TANAKA, TAKESHI HARADA, KOUICHI SAKAGUCHI and TAKEHIKO TANAKA, Department of Chemistry, Faculty of Science, Kyushu University 33, Hakozaki, Higashiku, Fukuoka 812, Japan.

- MG10 FOURIER-TRANSFORM MICROWAVE SPECTROSCOPY OF THE PROPARGYL RADICAL 15 min 4:16

KEIICHI TANAKA, Department of Chemistry, Faculty of Science, Kyushu University 33, Hakozaki, Higashiku, Fukuoka 812, Japan; YASUHIRO OHSHIMA and YASUKI ENDO, Department of Pure and Applied Science, College of Arts and Science, The University of Tokyo, Tokyo 153 Japan.

- MG11 FOURIER TRANSFORM MICROWAVE SPECTRA OF THE ALKALI HYDROXIDES GENERATED BY LASER ABLATION 10 min 4:33

Y. KAWASHIMA, Department of Chemical Technology, Kanagawa Institute of Technology 1030, Shimo-ogino, Atsugi, Kanagawa 243-02, Japan; R. D. SUENRAM, Molecular Physics, Division National Institute of Standards and Technology, Gaithersburg, Maryland 20899; and E. HIROTA, The Graduate University for Advanced Study, Nagatsuda, Midori-ku, Yokohama 227, Japan.

MG12 THE MOLECULAR BEAM OPTICAL STARK SPECTROSCOPY OF CALCIUM MONOHYDROSULFIDE; CaSH 15 min 4:45

C. T. SCURLOCK, T. HENDERSON, S. BOSELY, K. Y. JUNG and T. C. STEIMLE, Department of Chemistry, Arizona State University, Tempe AZ 85287-1604.

MG13 THE MILLIMETER-WAVE SPECTRUM OF CaSH 10 min 5:02

A. TALEB-BENDIAB, Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada; F. SCAPPINI, Istituto di Spettroscopia Molecolare del CNR Via de Castagnoli, 1-40126 Bologna, Italy; T. AMANO, Department of Physics and Astronomy, Ibaraki University, 2-1-1 Bunkyo, Mito 310, Japan; and J. K. G. WATSON, Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada.

MG14 A SUPERSONIC MOLECULAR BEAM STUDY OF CaNH₂ 10 min 5:14

K. Y. JUNG, B. -Z. LI and T. C. STEIMLE, Department of Chemistry, Arizona State University, Tempe AZ 85287-1604.

MONDAY, JUNE 13, 1994--1:30P.M.

ROOM 100 MCPHERSON LAB

Chair: MICHAEL C. HEAVEN, Emory University, Atlanta, Georgia

MH01	NEW BAND SYSTEM OF YbF MOLECULE	10 min	1:30
	<u>K. N. UTTAM</u> and M. M. JOSHI, Saha's Spectroscopy Laboratory, Physics Department, Allahabad University, Allahabad - 211002, India.		
MH02	ANALYSIS OF THE $A^2\Pi-X^2\Sigma^+$ TRANSITION IN YTTERBIUM MONOFLUORIDE	15 min	1:42
	<u>K. L. DUNFIELD</u> , T. E. CLARKE, C. LINTON, Physics Department, University of New Brunswick, Box 4400, Fredericton, N.B., Canada, E3B 5A3; A. G. ADAM and J. R. D. PEERS, Chemistry Department, University of New Brunswick, Fredericton, N.B., Canada, E3B 5A3.		
MH03	LASER SPECTROSCOPY OF YF: LINKAGE OF THE TRIPLET STATE MANIFOLD AT 0.03 cm^{-1} ACCURACY	10 min	1:59
	L. A. KALEDIN, <u>J. E. McCORD</u> and M. C. HEAVEN, Department of Chemistry, Emory University, Atlanta, GA 30322.		
MH04	LASER SPECTROSCOPY OF ScF: ANALYSIS OF PERTURBATIONS IN THE $F^1\Phi-A^1\Delta$ SYSTEM	10 min	2:11
	L. A. KALEDIN, <u>J. E. McCORD</u> and M. C. HEAVEN, Department of Chemistry, Emory University, Atlanta, GA 30322.		
MH05	HIGH RESOLUTION FOURIER TRANSFORM EMISSION SPECTROSCOPY OF YH AND YD	15 min	2:23
	<u>R. S. RAM</u> , Department of Chemistry, University of Arizona, Tucson, AZ 85721; and P. F. BERNATH, Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1.		
MH06	FOURIER TRANSFORM EMISSION SPECTROSCOPY OF THE $A^1\Sigma^+ - X^1\Sigma^+$ SYSTEM OF YN	10 min	2:40
	<u>R. S. RAM</u> , Department of Chemistry, University of Arizona, Tucson, AZ 85721; and P. F. BERNATH, Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1.		
MH07	FOURIER TRANSFORM EMISSION SPECTROSCOPY HfH AND HfD	10 min	2:52
	<u>R. S. RAM</u> , Department of Chemistry, University of Arizona, Tucson, AZ 85721; and P. F. BERNATH, Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1.		

INTERMISSION

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|------|--|--------|------|
| MH08 | HYPERFINE AND ISOTOPE STRUCTURE IN THE "ORANGE" SYSTEM OF FeO | 15 min | 3:20 |
| | <p>M. BARNES, M. M. FRASER, Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, B.C. Canada V6T 1Z1; P. G. HAJIGEORGIOU, Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1; and A. J. MERER, Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, B.C. Canada V6T 1Z1.</p> | | |
| MH09 | ELECTRONIC BAND SYSTEMS OF VCH IN THE 590-800 nm REGION | 15 min | 3:37 |
| | <p>M. BARNES, Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, B.C. Canada V6T 1Z1; P. G. HAJIGEORGIOU, Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1; A. J. MERER and G. F. METHA, Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, B.C. Canada V6T 1Z1.</p> | | |
| MH10 | THE OPTICAL SPECTRUM OF A SUPERSONIC MOLECULAR BEAM SAMPLE OF PtN | 15 min | 3:54 |
| | <p>K. Y. JUNG and T. C. STEIMLE, Department of Chemistry, Arizona State University, Tempe AZ 85287-1604.</p> | | |
| MH11 | THE VISIBLE SPECTRUM OF PLATINUM MONOSULFIDE; PtS | 10 min | 4:11 |
| | <p>B. -H. LI, and T. C. STEIMLE, Department of Chemistry, Arizona State University, Tempe AZ 85287-1604.</p> | | |
| MH12 | <i>Original abstract withdrawn - replaced by post-deadline abstract:</i>
LASER SPECTROSCOPY OF THE $A^4\Pi-X^4\Sigma^-$ TRANSITION OF MoN | 10 min | 4:23 |
| | <p>N. S -K. SZE and A. S -C. CHEUNG, Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong.</p> | | |
| MH13 | LASER PHOTOACOUSTIC SPECTROSCOPY OF Br ₂ VAPOUR IN THE YELLOW-GREEN REGION | 15 min | 4:35 |
| | <p>R. C. SHARMA and S. N. THAKUR, Laser and Spectroscopy Laboratory, Department of Physics, Banaras Hindu University, Varanasi-221 005, India.</p> | | |
| MH14 | MOLECULAR BEAM LASER SPECTROSCOPY OF THE COBALT MONOFLUORIDE MOLECULE | 15 min | 4:52 |
| | <p>A. G. ADAM, W. D. HAMILTON, S. MATTAR and M. C. STEEVES, Department of Chemistry, University of New Brunswick, Bag Service #45222, Fredericton, N.B., Canada, E3B 6E2.</p> | | |
| MH15 | LIF STUDY OF THE ELECTRONIC STATES AND SPECTRA OF BiF | 15 min | 5:09 |
| | <p>O. SHESTAKOV and E. H. FINK, Fachbereich Chemie, Universität Wuppertal, 42097 Wuppertal, F.R.G.</p> | | |

TUESDAY, JUNE 14, 1994--8:30A.M.

ROOM 1153 SMITH LAB

Chair: TIMOTHY C. STEIMLE, Arizona State University, Tempe, Arizona

TA01	THE B STATE OF THE SODIUM TRIMER: PSEUDOROTATION, AND CORIOLIS INTERACTION	15 min	8:30
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WOLFGANG E. ERNST and STEFAN RAKOWSKY, Department of Physics, The Pennsylvania State University, University Park, PA 16802.

TA02	HIGH RESOLUTION PHOTODETACHMENT SPECTROSCOPY OF CCCH_2^-	15 min	8:47
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K. YOKOYAMA, G. W. LEACH, J. B. KIM and W. C. LINEBERGER, Department of Chemistry and Biochemistry and Joint Institute for Laboratory Astrophysics, University of Colorado, Boulder, CO 80309.

TA03	HIGH RESOLUTION ELECTRONIC SPECTROSCOPY OF THE FS_2 FREE RADICAL	15 min	9:04
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DENNIS J. CLOUTHIER and Q. ZHUO, Department of Chemistry, University of Kentucky, Lexington, KY 40506-0055.

TA04	JET-COOLED SPECTROSCOPY OF Si_2N	10 min	9:21
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DALE J. BRUGH and MICHAEL D. MORSE, Department of Chemistry, University of Utah, Salt Lake City, UT 84112.

TA05	ELECTRONIC SPECTRA OF THE HETEROISOTOPIC CH_2D AND CD_2H RADICALS	15 min	9:33
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JEFFREY L. BRUM, RUSSELL D. JOHNSON III and JEFFREY W. HUDGENS, Chemical Kinetics and Thermodynamics Division, National Institute of Standards and Technology, Gaithersburg, MD 20899.

TA06	SPECTROSCOPY OF HALOGEN AMINE SYSTEMS: DISCHARGE FLOW METHODS AND LOW TEMPERATURE MATRIX ISOLATION	15 min	9:50
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YEVGENIYA I. GERSHANOVICH and JULANNA V. GILBERT, Department of Chemistry, University of Denver, Denver, CO 80208.

TA07	TRANSIENT FREQUENCY MODULATION SPECTROSCOPY	10 min	10:07
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GREGORY E. HALL, TREVOR J. SEARS, Department of Chemistry, P. O. Box 5000, Brookhaven National Laboratory, Upton, NY 11973-5000; JONATHAN C. BLOCH and ROBERT W. FIELD, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139.

TA08	NEAR-INFRARED ELECTRONIC TRANSIENT ABSORPTION SPECTRUM OF METHYLENE	10 min	10:19
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BOR-CHEN CHANG, MING WU, GREGORY E. HALL and TREVOR J. SEARS, Department of Chemistry, P. O. Box 5000, Brookhaven National Laboratory, Upton, NY 11973-5000.

INTERMISSION

TA09	LASER OPTOGALVANIC TRANSITIONS OF NEON IN THE NEAR ULTRAVIOLET AND VISIBLE	10 min	10:50
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P. MISRA, X. ZHU and A. H. NUR, Laser Spectroscopy Laboratory, Department of Physics & Astronomy, Howard University, Washington, D.C. 20059.

TA10	NEW ELECTRONIC STATES OF THE CHFCI RADICAL	15 min	11:02
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JEFFREY W. HUDGENS, RUSSELL D. JOHNSON III and BILIN P. TSAI, Chemical Kinetics and Thermodynamics Division, National Institute of Standards and Technology, Gaithersburg, MD 20899.

TA11	REMPI SPECTROSCOPY OF BF_2	15 min	11:19
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K. K. IRIKURA, R. D. JOHNSON III and J. W. HUDGENS, Chemical Kinetics and Thermodynamics Division, National Institute of Standards and Technology, Gaithersburg, MD 20899.

TA12	OBSERVATION OF TWO NEW ELECTRONIC STATES OF THE PCI_2 RADICAL	15 min	11:36
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JEFFREY W. HUDGENS and JEFFREY L. BRUM, Chemical Kinetics and Thermodynamics Division, National Institute of Standards and Technology, Gaithersburg, MD 20899.

TA13	A NEW ELECTRONIC STATE OF THE BCI RADICAL	15 min	11:53
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K. K. IRIKURA, J. W. HUDGENS and RUSSELL D. JOHNSON III, Chemical Kinetics and Thermodynamics Division, National Institute of Standards and Technology, Gaithersburg, MD 20899.

TA14	HIGH RESOLUTION SPECTROSCOPY OF THE $a^3\Pi_g-X^1\Sigma^+$ TRANSITION OF BCI	10 min	12:10
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K. I. MAHONEY, R. J. BRETT and C. W. MATHEWS, Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, Columbus, OH 43210.

TUESDAY, JUNE 14, 1994--8:30A.M.

ROOM 1009 SMITH LAB

Chair: TERRY L. GUSTAFSON, The Ohio State University, Columbus, Ohio

TB01	STRUCTURAL MEASUREMENTS OF ISOLATED CLUSTERS INVOLVING AROMATIC MOLECULES: OBSERVATION OF DIFFERENT ISOMERS AND VIBRONICALLY INDUCED PHOTOISOMERIZATION (<i>INVITED</i>)	30 min	8:30
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T. TROXLER, J. R. STRATTON, P. G. SMITH and M. R. TOPP, Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104-6323.

TB02	STRUCTURAL DETERMINATION OF VAN DER WAALS COMPLEXES OF PERYLENE WITH CYCLOPROPANE USING ROTATIONAL COHERENCE SPECTROSCOPY	15 min	9:05
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J. R. STRATTON, T. TROXLER and M. R. TOPP, Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104-6323.

TB03	SPECTROSCOPIC OBSERVATIONS OF IVR THRESHOLDS IN MOLECULES WITH INTERNAL ROTATION	15 min	9:22
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Q. JU, S. -P. LU, T. A. STONE, C. S. PARMENTER, Department of Chemistry, Indiana University, Bloomington, IN 47405; and Z. -Q. ZHAO, JILA, University of Colorado, Boulder, CO 80309.

TB04	DEEP ULTRAVIOLET FEMTOSECOND MPI STUDIES OF EXCITED STATE DYNAMICS OF NITRIC OXIDE AND CARBON DISULFIDE	15 min	9:39
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J. C. OWRUTSKY and A. P. BARONAVSKI, Code 6111, Chemistry Division, Naval Research Laboratory, Washington, D.C. 20375.

TB05	LIFETIMES OF THE \tilde{B} STATE OF CH_3I AND CD_3I USING FEMTOSECOND RESONANCE ENHANCED MULTIPHOTON IONIZATION	15 min	9:56
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A. P. BARONAVSKI and J. C. OWRUTSKY, Code 6111, Chemistry Division, Naval Research Laboratory, Washington, D.C. 20375.

INTERMISSION

TB06	FEMTOSECOND MID-IR SPECTROSCOPY USED TO PROBE THE ULTRAFAST DYNAMICS OF LIGAND MOTION SUBSEQUENT TO PHOTODISSOCIATION OF CARBONMONOXYMYOGLOBIN	15 min	10:30
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T. A. JACKSON, M. LIM and P. A. ANFINRUD, Department of Chemistry, Harvard University, Cambridge, MA 02138.

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| TB07 | DETERMINATION OF THE ORIENTATION OF CARBON MONOXIDE IN THE HEME POCKET OF MYOGLOBIN IN SOLUTION USING TIME-RESOLVED MID-INFRARED SPECTROSCOPY | 15 min | 10:47 |
| | <u>M. LIM</u> , T. JACKSON and P. ANFINRUD, Department of Chemistry, Harvard University, Cambridge, MA 02138. | | |
| TB08 | THEORETICAL CALCULATION OF PUMP-PROBE STIMULATED EMISSION PROFILES OF ULTRAFAST ELECTRON TRANSFER | 10 min | 11:04 |
| | <u>S. SUZUKI</u> , M. HAYASHI, X. GU and S. H. LIN, Department of Chemistry and Biochemistry, Arizona State University, Tempe, AZ 85287-1604. | | |
| TB09 | SOLVENT/SOLUTE INTERACTIONS PROBED BY PICOSECOND TRANSIENT RAMAN SPECTROSCOPY | 15 min | 11:16 |
| | <u>D. L. MORRIS</u> and T. L. GUSTAFSON, Department of Chemistry, The Ohio State University, 120 W. 18th Ave., Columbus, OH 43210. | | |
| TB10 | SOLVENT-SOLUTE INTERACTIONS PROBED BY PICOSECOND TRANSIENT RAMAN SPECTROSCOPY: EXCITATION ENERGY EFFECTS AND SOLVENT DEPENDENCE OF S ₁ TRANS-4,4'-DIPHENYLSTILBENE | 15 min | 11:33 |
| | <u>J. D. LEONARD, JR.</u> and T. L. GUSTAFSON, Department of Chemistry, The Ohio State University, 120 W. 18th Ave., Columbus, OH 43210. | | |
| TB11 | RESONANCE RAMAN STUDIES ON EXCITED STATES OF Zn(II) OCTAETHYLPORPHYRIN | 15 min | 11:50 |
| | <u>G. DEINUM</u> , D. H. KRESZOWSKI and G. T. BABCOCK, Department of Chemistry and the LASER Laboratory, Michigan State University, East Lansing, MI 48824. | | |
| TB12 | ULTRAFAST SPONTANEOUS AND STIMULATED EMISSION SPECTROSCOPY OF COUMARIN 153: EVIDENCE FOR THE EXISTENCE OF MULTIPLE EXCITED ELECTRONIC STATES | 15 min | 12:07 |
| | <u>G. J. BLANCHARD</u> , Y. JIANG and P. K. MCCARTHY, Department of Chemistry, Michigan State University, East Lansing, MI 48824. | | |

TUESDAY, JUNE 14, 1994--8:30A.M.

ROOM 1005 SMITH LAB

Chair: HENRY O. EVERITT, U. S. Army Research Office, Durham, North Carolina

TC01	THE MICROWAVE SPECTRUM AND STRUCTURE OF THE DIMETHYLAMINE DIMER: EVIDENCE FOR A CYCLIC STRUCTURE	15 min	8:30
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MICHAEL J. TUBERGEN and ROBERT L. KUCZKOWSKI, Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109-1055.

TC02	HYDROGEN BONDING TO DIMETHYLAMINE: THE MICROWAVE SPECTRUM AND STRUCTURE OF THE DIMETHYLAMINE-WATER COMPLEX	10 min	8:47
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MICHAEL J. TUBERGEN and ROBERT L. KUCZKOWSKI, Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109-1055.

TC03	ROTATIONAL SPECTRUM AND STRUCTURE OF THE BENZENE-HCN DIMER	10 min	8:59
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H. S. GUTOWSKY, E. ARUNAN, T. EMILSSON and S. L. TSCHOPP, Department of Chemistry, University of Illinois, Urbana, IL 61801.

TC04	ROTATIONAL SPECTRA AND STRUCTURES OF Rg-C ₆ H ₆ -H ₂ O SANDWICH TRIMERS (Rg = Ne, Ar, or Kr)	15 min	9:11
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E. ARUNAN, T. EMILSSON and H. S. GUTOWSKY, Department of Chemistry, University of Illinois, Urbana, IL 61801.

TC05	THE MICROWAVE SPECTRUM AND r_0 STRUCTURE OF THE FURAN ...H ₂ O COMPLEX, A CASE OF LARGE AMPLITUDE MOTION	15 min	9:28
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F. L. BETTENS, R. P. A. BETTENS, Department of Physics, Ohio State University, Columbus, Ohio 43210; and A. BAUDER, Laboratorium für Physikalische Chemie, Eidgenössische Technische Hochschule, CH-8092 Zürich, Switzerland.

TC06	CENTRIFUGAL DISTORTION ANALYSIS OF RARE GAS ...AROMATIC MOLECULE COMPLEXES	15 min	9:45
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R. P. A. BETTENS, Department of Physics, Ohio State University, Columbus, Ohio 43210; R. M. SPYCHER and A. BAUDER, Laboratorium für Physikalische Chemie, Eidgenössische Technische Hochschule, CH-8092 Zürich, Switzerland.

INTERMISSION

TC07	NOVEL CYCLOPROPANE COMPLEXES: CYCLOPROPANE•AMMONIA AND CYCLOPROPANE•TRIMETHYLAMINE	15 min	10:20
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SUSAN E. FOREST and ROBERT L. KUCZKOWSKI, Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109-1055.

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| TC08 | EXCITED $\nu_3(\text{HCN})$ VIBRATIONAL STATE OF THE Rg-HCN DIMERS ($\text{Rg} = \text{Ar}, \text{Kr}$) | 10 min | 10:37 |
| | <u>E. ARUNAN</u> , T. EMILSSON and H. S. GUTOWSKY, Department of Chemistry, University of Illinois, Urbana, IL 61801. | | |
| TC09 | MICROWAVE STUDIES OF ARGON COMPLEXES WITH FULMINIC ACID AND ISOCYANIC ACID | 15 min | 10:49 |
| | C. BOYCE, <u>C. W. GILLIES</u> , Department of Chemistry, Rensselaer Polytechnic Institute, Troy, NY 12180; J. Z. GILLIES, Department of Chemistry, Siena College, Loudonville, NY 12221; F. J. LOVAS, R. D. SUENRAM, Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, MD 20899; and H. E. WARNER, Department of Chemistry, Rensselaer Polytechnic Institute, Troy, NY 12180. | | |
| TC10 | THE MICROWAVE SPECTRUM, STRUCTURE AND TUNNELING MOTION OF THE ARGON-KETENE VAN DER WAALS COMPLEX | 10 min | 11:06 |
| | R. MOLLOY, <u>C. W. GILLIES</u> , Department of Chemistry, Rensselaer Polytechnic Institute, Troy, NY 12180; J. Z. GILLIES, Department of Chemistry, Siena College, Loudonville, NY 12221; F. J. LOVAS and R. D. SUENRAM, Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, MD 20899. | | |
| TC11 | ROTATIONAL SPECTRA AND INTERNAL DYNAMICS OF $\text{Ar}_2\text{-H}_2\text{O}$, $\text{Ar}_3\text{-H}_2\text{O}$, AND $\text{Ar-(H}_2\text{O)}_3$ | 15 min | 11:18 |
| | <u>E. ARUNAN</u> , T. EMILSSON and H. S. GUTOWSKY, Department of Chemistry, University of Illinois, Urbana, IL 61801. | | |
| TC12 | THE MICROWAVE SPECTRUM AND STRUCTURE OF THE $\text{CH}_3\text{CN-H}_2\text{O}$ AND $\text{CH}_3\text{OH-HCN}$ DIMERS | 15 min | 11:35 |
| | <u>F. J. LOVAS</u> , Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, MD 20899; and J. SOBHANADRI, Department of Physics, Indian Institute of Technology, Madras, 600036, India. | | |
| TC13 | THE MICROWAVE SPECTRUM AND STRUCTURE OF THE $\text{CH}_3\text{NO}_2\text{-H}_2\text{O}$ DIMER | 15 min | 11:52 |
| | <u>F. J. LOVAS</u> , Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, MD 20899; N. ZOBOV, Molecular Spectroscopy Laboratory, Applied Physics Institute, 46 Ulyanova St., Nizhnii Novgorod, Russia 603024 (Formerly Gorky, USSR); W. J. STEVENS, Center for Advanced Research in Biotechnology, National Institute of Standards and Technology, Gudelsky Dr., Rockville, MD 20850; G. T. FRASER and R. D. SUENRAM, Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, MD 20899. | | |

TUESDAY, JUNE 14, 1994--8:30A.M.

ROOM 100 MCPHERSON LAB

Chair: BRENDA P. WINNEWISSER, Justus-Liebig-Universität, Giessen, Germany

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| TD01 | CH ₃ ¹⁸ OH: A REVIEW OF FIR LASER LINE MEASUREMENTS AND ASSIGNMENTS | 15 min | 8:30 |
| | <p>S. ZHAO, <u>R. M. LEES</u>, CEMAID and Physics Department, University of New Brunswick, Fredericton, N.B., Canada E3B 5A3; R. R. J. GOULDING, Department of Physics, Memorial University of Newfoundland, St. John's, Nfld., Canada A1B 3X7; G. CARELLI, N. IOLI, A. MORETTI, G. MORUZZI and F. STRUMIA, Dipartimento di Fisica dell'Università di Pisa, Piazza Torricelli 2, I-56126 Pisa, Italy.</p> | | |
| TD02 | NEW FIR LASER EMISSIONS FOR METHANOL ISOTOPOMERS PUMPED WITH THE NEW BOULDER CO ₂ LASER | 15 min | 8:47 |
| | <p><u>LI-HONG XU</u>, Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899; R. M. LEES, CEMAID and Physics Department, University of New Brunswick, Fredericton, N.B., Canada E3B 5A3; E. C. C. VASCONCELLOS, Instituto de Fisica, Depto. de Eletrônica Quântica, UNICAMP, 13083-970 Campinas, SP, Brazil; and K. M. EVENSON, Time and Frequency, National Institute of Standards and Technology, Boulder, CO 80303.</p> | | |
| TD03 | FIR LASER ASSIGNMENTS FOR HYDRAZINE BY FOURIER TRANSFORM SPECTROSCOPY | 15 min | 9:04 |
| | <p><u>LI-HONG XU</u>, J. T. HOUGEN, Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899; J. W. C. JOHNS, and Z. F. LU, Herzberg Institute of Astrophysics, N.R.C., Ottawa, Ont., Canada K1A 0R6.</p> | | |
| TD04 | A NEW "RITZ" PROGRAM FOR DIRECT ENERGY LEVEL FITTING AND FIR LASER LINE PREDICTION | 15 min | 9:21 |
| | <p><u>G. MORUZZI</u>, Dipartimento di Fisica dell'Università di Pisa, Piazza Torricelli 2, I-56100 Pisa, Italy; and <u>LI-HONG XU</u>, Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899.</p> | | |
| TD05 | A WAVELENGTH METER FOR INFRARED DIODE LASER | 10 min | 9:38 |
| | <p><u>EIZI HIROTA</u>, The Graduate University for Advanced Studies, 4259 Nagatsuta, Midori, Yokohama 227, Japan; KAZUO HAYAKAWA, Shizuoka Institute of Science and Technology, 2200-2 Toyosawa, Fukuroi, Shizuoka 437, Japan; MISAKI OKUNISHI, Research Institute for Scientific Measurements, Tohoku University, 2-1-1 Katahira, Aoba, Sendai 980, Japan; and CHIKASHI YAMADA, Optoelectronics Technology Research Laboratory, 5-5 Tohkodai, Tsukuba 300-26, Japan.</p> | | |

TD06 AUTOMATED WAVENUMBER DETERMINATION FOR DIODE LASER SPECTRA 15 min 9:50

LI-HONG XU, Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899; R. M. LEES, CEMAD and Physics Department, University of New Brunswick, Fredericton, N.B., Canada E3B 5A3; and G. MORUZZI, Dipartimento di Fisica dell'Università di Pisa, Piazza Toricelli 2, I-56126 Pisa, Italy.

INTERMISSION

TD07 PULSED MILLIMETER AND SUBMILLIMETER WAVE GENERATION 15 min 10:20

W. GUO, Department of Physics, The Ohio State University, 174 West 18th Avenue, Columbus, OH 43210-1106; J. C. SWARTZ, Department of Physics, Duke University, Durham, NC 27706; J. M. DUTTA, C. R. JONES, Department of Physics, North Carolina Central University, Durham NC 27707; B. D. GUENTHER, Department of Physics, Duke University, Durham, NC 27706; and F. C. DE LUCIA, Department of Physics, The Ohio State University, 174 West 18th Avenue, Columbus, OH 43210-1106.

TD08 ORIENTATION MODULATION IN FOUR-LEVEL INFRARED-INFRARED DOUBLE RESONANCE IN METHYL FLUORIDE AND AMMONIA 15 min 10:37

GLENDA M. SORIANO and R. H. SCHWENDEMAN, Department of Chemistry, Michigan State University, East Lansing, MI 48824.

TD09 STARK SPECTROSCOPY USING THE WATER VAPOR LASER 15 min 10:54

M. JACKSON, Department of Physics, New Mexico State University, Las Cruces, NM 88003; G. R. SUDHAKARAN, Department of Physics, SUNY at Oswego, Oswego, NY 13126 (present address: Department of Physics, University of Wisconsin, La Crosse, WI 54601); R. M. LEES, Department of Physics, University of New Brunswick, Fredericton, New Brunswick, Canada E3B5A3; and I. MUKHOPADHYAY, Laser Program, Center for Advanced Technology, Indore 452 013, M. P., India.

TD10 DIODE-LASER MOLECULAR BEAM SPECTRUM OF THE ν_2 NO STRETCHING BAND OF CHLORINE NITRATE 15 min 11:11

ANNE M. ANDREWS, Molecular Physics Division, NIST, Gaithersburg, MD 30899; JOSÉ L. DOMENECH, Instituto de Estructura de la Materia, C.S.I.C., Serano 119, Madrid, Spain; GERALD T. FRASER, WALTER J. LAFFERTY, RICHARD D. SUENRAM, Molecular Physics Division, NIST, Gaithersburg, MD 30899; and PATRICIA WATSON, Dupont Central Research and Development Laboratory, Wilmington, DE 19880.

TD11 ACCURATE FAR-INFRARED FREQUENCIES FOR PURE ROTATIONAL AND FINE-STRUCTURE TRANSITIONS IN THE $^2\Pi$ ELECTRONIC GROUND STATE OF NITRIC OXIDE, NO 15 min 11:28

F. STROH, NIST, Time and Frequency Division, 325 Broadway, Boulder CO 80303; T. D. VARBERG, Department of Chemistry, Macalester College, St. Paul, MN 55105; and K. M. EVENSON, NIST, Time and Frequency Division, 325 Broadway, Boulder CO 80303.

TD12 ROVIBRATIONAL ENERGY TRANSFER IN HIGHLY VIBRATIONALLY EXCITED CH₄

15 min 11:45

JODY KLAASSEN, STEVE COY, ILYA DUBINSKY, JEFF STEINFELD,
Department of Chemistry, M.I.T., Cambridge, MA 02139; and BERND ABEL,
Universität of Göttingen, Germany.

TUESDAY, JUNE 14, 1994--1:30P.M.

ROOM 1153 SMITH LAB

Chair: WALTER J. LAFFERTY, National Institute of Standards and Technology, Gaithersburg, Maryland

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|------|---|--------|------|
| TE01 | ROVIBRATIONAL SPECTRA OF THE STRETCHING FUNDAMENTAL OF CCl ₄ | 15 min | 1:30 |
| | <u>SONGLIN XU</u> , R. S. McDOWELL and S. W. SHARPE, Molecular Science Research Center, Battelle Pacific Northwest Laboratory, Richland, WA 99352. | | |
| TE02 | SUB-DOPPLER OPTOTHERMAL SPECTROSCOPY AND INTRAMOLECULAR DYNAMICS OF THE ν_1 AND $2\nu_1$ BANDS OF SF ₆ CCH | 15 min | 1:47 |
| | M. BECUCCI, Laboratorio Europeo di Spettoscopia Non-lineari (LENS), Largo E. Fermi No. 2 (Arcetri), 50125 Firenze, Italy; J. E. GAMBOGI, J. H. TIMMERMANS, <u>K. K. LEHMANN</u> , G. SCOLES, Department of Chemistry, Princeton University, Princeton, NJ 08544; and G. L. GARD, Department of Chemistry, Portland State University, Portland, OR 97027. | | |
| TE03 | INTRACAVITY LASER ABSORPTION SPECTROSCOPY IN THE NEAR INFRARED WITH DOPPLER LIMITED RESOLUTION | 15 min | 2:04 |
| | <u>A. KACHANOV</u> , Institute for Spectroscopy, 142092 Troitsk, Moscow region, Russia; B. ABEL, J. TROE, Institute for Physical Chemistry, University of Goettingen, 37077 Goettingen, Germany; and F. STOECKEL, Laboratoire de Spectrométrie Physique, Université Joseph Fourier de Grenoble/CNRS URA 08 B.P. 87 38402 Saint-Martin-d'Hères Cedex France. | | |
| TE04 | DEVELOPMENT, JUSTIFICATION AND APPLICATIONS OF A MID-INFRARED POLARIZATION DIVISION INTERFEROMETER | 15 min | 2:21 |
| | <u>PRASAD L. POLAVARAPU</u> , GANG-CHI CHEN, Department of Chemistry, Vanderbilt University, Nashville, TN 37235; and STEPHEN WEIBEL, ATI Instruments N.A., 1001 Fourier Drive, Madison, WI 53717. | | |
| TE05 | POLARIZATION DIVISION INTERFEROMETRY: FAR INFRARED DICHROISM | 15 min | 2:38 |
| | <u>PRASAD L. POLAVARAPU</u> , GANG-CHI CHEN, Department of Chemistry, Vanderbilt University, Nashville, TN 37235. | | |
| TE06 | POLARIZATION DIVISION INTERFEROMETRY: TIME RESOLVED INFRARED DICHROISM | 15 min | 2:55 |
| | <u>PRASAD L. POLAVARAPU</u> , GANG-CHI CHEN, Department of Chemistry, Vanderbilt University, Nashville, TN 37235. | | |

TUESDAY, JUNE 14, 1994-3:30P.M.

ROOM 1153 SMITH LAB

Chair: EIZI HIROTA, Graduate University for Advanced Studies, Yokohama, Japan

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| TE'01 | FINE AND HYPERFINE STRUCTURE OF THE X $^2\Pi_0$ ELECTRONIC STATE OF HBr ⁺ | 15 min | 3:30 |
| | <u>A. CHANDA</u> , W. C. HO, F. W. DALBY and I. OZIER, Department of Physics, University of British Columbia, Vancouver, B.C., Canada V6T 1Z1. | | |
| TE'02 | FIRST HIGH RESOLUTION SPECTROSCOPIC STUDY OF THE X $^2\Pi_0$ ELECTRONIC STATE OF HI ⁺ : FINE AND HYPERFINE STRUCTURE ANALYSIS OF THE VIBRATION-ROTATION SPECTRUM | 15 min | 3:47 |
| | <u>A. CHANDA</u> , W. C. HO, F. W. DALBY and I. OZIER, Department of Physics, University of British Columbia, Vancouver, B.C., Canada V6T 1Z1. | | |
| TE'03 | INFRARED ABSORPTION SPECTROSCOPY OF JET-COOLED MOLECULAR IONS | 15 min | 4:04 |
| | MASARU FUKUSHIMA, Advanced Technology Research Center, Mitsubishi Heavy Industries Ltd., 8-1, Sachiura 1, Kanazawa, Yokohama 236, Japan; <u>MAN-CHOR CHAN</u> , Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27599; YUNJIE XU, AMINE TALEB-BENDIAB, Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Canada, K1A 0R6; and TAKAYOSHI AMANO, Department of Physics, Ibaraki University, 2-1-1 Bunkyo, Mito 310, Japan. | | |
| TE'04 | NEAR-INFRARED DIODE LASER ABSORPTION SPECTROSCOPY OF THE JET-COOLED N $_2^+$ ION | 10 min | 4:21 |
| | <u>KENSUKE HARADA</u> and TAKEHIKO TANAKA, Department of Chemistry, Faculty of Science, Kyushu University 33, Hakozaki, Higashiku, Fukuoka 812, Japan. | | |
| TE'05 | CARBO-ION SPECTROSCOPY WITH TUNABLE DIODE LASERS: THE BENDING VIBRATIONS OF CH $_3^+$ | 15 min | 4:33 |
| | <u>SANGWOO JOO</u> , FRANK KÜHNEMANN and TAKESHI OKA, Department of Chemistry and Department of Astronomy and Astrophysics, The University of Chicago, Chicago IL 60637-1403. | | |
| TE'06 | INFRARED STUDIES OF THE ν_3 BAND OF CH $_2^+$ | 15 min | 4:50 |
| | <u>CHARLES GABRYS</u> , DAIRENE UY, MARY-FRANCES JAGOD and TAKESHI OKA, University of Chicago, Department of Chemistry, 5735 S. Ellis, Chicago, IL 60637-1403. | | |

TE'07 MILLIMETER-WAVE LABORATORY DETECTION OF H_2COH^+ 15 min 5:07

D. CHOMIAK, A. TALEB-BENDIAB, Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada; S. CIVIŠ, J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, 182 23 Prague 8, Dolejškova 3, The Czech Republic; and T. AMANO, Department of Physics and Astronomy, Ibaraki University, 2-1-1 Bunkyo, Mito 310, Japan.

TE'08 MEASUREMENT BY MILLIMETER-WAVE SPECTROSCOPY OF TUNNELING SPLITTING FOR THE NON-CLASSICAL FORM OF C_2H_3^+ 15 min 5:24

M. BOGEY, Laboratoire de Spectroscopie Hertzienne, U.F.R. de Physique, Université de Lille I, Villeneuve d'ascq, F-59655, France; M. CORDONNIER, Department of Chemistry, University of Chicago, 5735 S. Ellis Ave., Chicago, IL 60637; C. DEMUYNCK and J. L. DESTOMBES, Laboratoire de Spectroscopie Hertzienne, U.F.R. de Physique, Université de Lille I, Villeneuve d'ascq, F-59655, France.

TUESDAY, JUNE 14, 1994--1:30P.M.

ROOM 1009 SMITH LAB

Chair: JOYCE A. GUEST, University of Cincinnati, Cincinnati, Ohio

TF01	OBSERVATION OF INTERVALLENCE TRANSITIONS OF NAPHTHALENE CLUSTERS AND THEIR CATIONS BY PHOTODISSOCIATION SPECTROSCOPY	15 min	1:30
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HIROYUKI SAIGUSA and E. C. LIM, Department of Chemistry, The University of Akron, Akron, OH 44325-3601.

TF02	SPECTRAL HOLE BURNING AS PROBE OF INTERMOLECULAR VIBRATIONS IN HYDROGEN BONDED MOLECULAR COMPLEXES	15 min	1:47
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M. SCHMITT, H. MÜLLER, K. KLEINERMANN, Institut für Physikalische Chemie I, Heinrich-Heine-Universität Düsseldorf, Universitätsstr. 26.43 D-40225 Düsseldorf.

TF03	ZEKE SPECTROSCOPIC STUDIES OF HYDROGEN-BONDED PHENOL COMPLEXES	15 min	2:04
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TIMOTHY G. WRIGHT, Laser Spectroscopy Facility, Chemistry Department, The Ohio State University, Columbus, Ohio 43210; OTTO DOPFER, ERIC CORDES, GERHARD LEMBACH and KLAUS MÜLLER-DETHLEFS, Institut für Physikalische Chemie der Technischen Universität München, Lichtenberstr. 4, 85747 Garching, Germany.

TF04	EMISSION FROM THE PRODUCTS OF THE MULTIPHOTON DISSOCIATION OF KETENE AND ACETYL BROMIDE	15 min	2:21
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Z. LI, Jet Propulsion Laboratory 183-901, 4800 Oak Grove Drive, Pasadena, CA 91109; T. S. DIBBLE, Y. SU, J. S. FRANCISCO, Department of Chemistry, Wayne State University, Detroit, MI 48202; M. M. MARICQ and J. J. SZENTE, Research Laboratory, Ford Motor Company, Dearborn, Michigan 48121.

TF05	HIGH RESOLUTION, ROTATIONALLY RESOLVED ELECTRONIC SPECTRA OF CaC_3H_5	15 min	2:38
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TIMOTHY M. CERNY, JAMES M. WILLIAMSON and TERRY A. MILLER, Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, 120 West 18th Avenue, Columbus, Ohio 43210.

TF06	METHANE VAN DER WAALS COMPLEXES OF THE FLUORONAPHTHALENES. A PERTURBED SPHERICAL TOP ATTACHED TO A SURFACE	15 min	2:55
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J. F. PFANSTIEL, B. B. CHAMPAGNE and D. W. PRATT, Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260.

INTERMISSION

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| TF07 | METHYL INTERNAL ROTATION IN THE S_1 STATE OF 2-CHLORO-6-FLUOROTOLUENE: EXPERIMENT AND THEORY | 15 min | 3:30 |
| | <p><u>E. C. RICHARD</u>, R. A. WALKER, Department of Chemistry, University of Wisconsin, Madison, WI 53706; K-T. LU, Department of Chemistry, University of California at Berkeley, Berkeley, CA 94720; and J. C. WEISSHAAR, Department of Chemistry, University of Wisconsin, Madison, WI 53706.</p> | | |
| TF08 | LOW ENERGY INTERNAL ROTATION IN THE S_1 AND GROUND CATION STATES OF 2,6-DIFLUOROTOLUENE | 15 min | 3:47 |
| | <p><u>R. A. WALKER</u>, E. C. RICHARD, Department of Chemistry, University of Wisconsin, Madison, WI 53706; K-T. LU, Department of Chemistry, University of California at Berkeley, Berkeley, CA 94720; and J. C. WEISSHAAR, Department of Chemistry, University of Wisconsin, Madison, WI 53706.</p> | | |
| TF09 | FAR-INFRARED SPECTRA AND TWO-DIMENSIONAL POTENTIAL ENERGY SURFACES FOR THE OUT-OF-PLANE RING VIBRATIONS OF CYCLOPENTANONE IN ITS S_0 AND $S_1(n, \pi)$ ELECTRONIC STATES | 15 min | 4:04 |
| | <p>JAEBUM CHOO and <u>JAAN LAANE</u>, Department of Chemistry, Texas A&M University, College Station, Texas 77843-3255.</p> | | |
| TF10 | SPECTROSCOPY AND CONFORMATION OF A SERIES OF BENZYLIDENE CYCLOALKANES | 15 min | 4:21 |
| | <p><u>J. R. CABLE</u>, N. WESTRICK, V. MANEA, Department of Chemistry and Center for Photochemical Sciences, Bowling Green State University, Bowling Green, OH 43403.</p> | | |
| TF11 | AN AB-INITIO CALCULATION OF THE $S_0 \rightarrow S_1$ TRANSITION OF ANTHRACENE AND ITS VIBRONIC STRUCTURE | 15 min | 4:38 |
| | <p><u>Y. HAAS</u>, S. ZILBERG, U. SAMUNI and R. FRANKEL, Department of Physical Chemistry and the Farkas Center for Light Induced Processes, The Hebrew University of Jerusalem 91904, Israel.</p> | | |
| TF12 | SUPERSONIC JET SPECTRA OF PARA SUBSTITUTED ANILINES | 10 min | 4:55 |
| | <p>S. WATEGAONKAR and <u>S. DORAISWAMY</u>, Chemical Physics Group, Tata Institute of Fundamental Research, Homi Bhabha Road, Colaba, Bombay 400 005 (India).</p> | | |
| TF13 | <i>Post-deadline Abstract</i>
FLUORESCENCE SPECTRA AND TORSIONAL POTENTIAL FUNCTIONS FOR <i>TRANS</i> -STILBENE IN ITS S_0 AND $S_1(\pi, \pi^*)$ ELECTRONIC STATES | 15 min | 5:07 |
| | <p>WHE-YI CHIANG and <u>JAAN LAANE</u>, Department of Chemistry, Texas A&M University, College Station, Texas 77843-3255.</p> | | |

TF14 *Post-deadline Abstract*

15 min

5:24

TRIPLET STATE ELECTRONIC STRUCTURE OF ZINC (II)
TETRAPHENYLPORPHYRINS

V. A. WALTERS, Department of Chemistry, Lafayette College, Easton, PA 18042; J. C. DE PAULA, B. JACKSON, Department of Chemistry, Haverford College, Haverford, PA 19041; C. NUTAITIS, K. HALL, Department of Chemistry, Lafayette College, Easton, PA 18042; J. LIND, K. CARDOZO, Department of Chemistry, Haverford College, Haverford, PA 19041; K. CHANDRAN, D. RAIBLE, Department of Chemistry, Lafayette College, Easton, PA 18042; and C. M. PHILLIPS, Regional Laser and Biotechnology Laboratory, University of Pennsylvania, Philadelphia, PA 19104.

TUESDAY, JUNE 14, 1994--1:30P.M.

ROOM 1005 SMITH LAB

Chair: MARILYN E. JACOX, National Institute of Standards and Technology, Gaithersburgh, Maryland

TG01	GROUND STATE OF THE NbH ₂ MOLECULE IN RARE GAS AND DEUTERIUM MATRICES	10 min	1:30
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R. J. VAN ZEE, S. LI, and W. WELTNER, JR., Department of Chemistry,
University of Florida, Gainesville, FL 32611-2046.

TG02	INFRARED SPECTRA OF Si ₂ , Ge ₂ , Sn ₂ , SiGe, AND SiSn MOLECULES IN RARE-GAS MATRICES: ELECTRONIC TRANSITIONS AND MAGNETIC EFFECTS	10 min	1:42
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S. LI, R. J. VAN ZEE, and W. WELTNER, JR., Department of Chemistry,
University of Florida, Gainesville, FL 32611-2046.

TG03	REACTIONS OF LASER ABLATED Ti ATOMS WITH HYDROGEN DURING CONDENSATION IN EXCESS ARGON. INFRARED SPECTRA OF THE TiH, TiH ₂ , TiH ₃ AND TiH ₄ MOLECULES	15 min	1:54
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GEORGE V. CHERTIHIN and LESTER ANDREWS, Department of Chemistry,
University of Virginia, Charlottesville, VA 22901.

TG04	REACTIONS OF LASER ABLATED Be ATOMS WITH O ₂ : INFRARED SPECTRA OF BERYLLIUM OXIDES IN SOLID ARGON	15 min	2:11
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CRAIG A. THOMPSON and LESTER ANDREWS, Department of Chemistry,
University of Virginia, Charlottesville, VA 22901.

TG05	PULSED-LASER EVAPORATED MAGNESIUM ATOM REACTIONS WITH HYDROGEN: INFRARED SPECTRA OF FIVE MAGNESIUM HYDRIDE PRODUCT MOLECULES	15 min	2:28
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THOMAS J. TAGUE JR., Bruker Instruments, Inc., Fortune Drive, Manning Park,
Billerica, MA 01821; and LESTER ANDREWS, Department of Chemistry, University
of Virginia, Charlottesville, VA 22901.

TG06	FTIR OBSERVATION OF VIBRATIONAL FUNDAMENTALS FOR SMALL SILICON CLUSTERS TRAPPED IN SOLID ARGON	15 min	2:45
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SHUNLIN WANG, C. M. L. RITBY and W. R. M. GRAHAM, Department of
Physics, Texas Christian University, Fort Worth, TX 76129.

TG07	Original abstract withdrawn - replaced by post-deadline abstract: PHOTOCHEMISTRY AND SPECTROSCOPY OF MATRIX ISOLATED C ₃ •H ₂ O COMPLEX	15 min	3:02
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J. SZCZEPANSKI, S. EKERN and M. VALA, Department of Chemistry, University
of Florida, Gainesville, FL 32611.

INTERMISSION

TG08	FTIR SPECTROSCOPY OF MASS-SELECTED, MATRIX-ISOLATED CATIONS	15 min	3:40
	<u>J. T. GODBOUT</u> , T. M. HALASINSKI, J. ALLISON and G. E. LEROI, Department of Chemistry, Michigan State University, East Lansing, MI 48824-1322.		
TG09	ABSOLUTE INFRARED INTENSITY MEASUREMENTS FOR MATRIX-ISOLATED SAMPLES	15 min	3:57
	<u>WILLIS B. PERSON</u> , KRYSTYNA SZCZEPANIAK, Department of Chemistry, University of Florida, Gainesville, FL 32611; and JANET E. DEL BENE, Department of Chemistry, Youngstown State University, Youngstown, OH 44555.		
TG11	MIXING OF ATOMIC RYDBERG AND MOLECULAR CHARGE TRANSFER STATES OF FLUORINE ATOMS IN A NEON MATRIX	15 min	4:14
	C. B. BRESSLER, Institut Fur Experimentalphysik, Freie Universitat Berlin, D-14195 Berlin Germany; <u>W. G. LAWRENCE</u> , Department of Chemistry, Emory University, Atlanta, GA 30322; and N. SCHWENTNER, Institut Fur Experimentalphysik, Freie Universitat Berlin, D-14195 Berlin Germany.		
TG12	MANY BODY POTENTIALS OF AN OPEN SHELL ATOM: SPECTROSCOPY OF SPIN-ORBIT TRANSITIONS OF IODINE IN CRYSTALLINE Xe AND Kr	15 min	4:31
	<u>W. G. LAWRENCE</u> , Department of Chemistry, Emory University, Atlanta, GA 30322; and V. A. APKARIAN, Department of Chemistry, University of California Irvine, Irvine CA.		
TG13	MORPHOLOGY EFFECTS ON THE SPECTROSCOPY AND DYNAMICS OF HCl IN AN ARGON MATRIX	10 min	4:48
	H. -S. LIN, <u>W. G. LAWRENCE</u> and M. C. HEAVEN, Department of Chemistry, Emory University, Atlanta, GA 30322.		
TG14	SIMULATIONS OF KRYPTON MATRIX EFFECTS ON THE ELECTRONIC SPECTRUM OF Na ₂	10 min	5:00
	<u>A. V. NEMUKHIN</u> , B. L. GRIGORENKO, and G. B. SERGEEV, Department of Chemistry, Moscow State University, Moscow 119899 GSP Russia.		
TG15	INTERACTION OF TRAPPED H(D) ATOMS WITH Xe MATRIX INFLUENCED BY ZERO-POINT VIBRATIONS OF THE LIGHT ATOMS	15 min	5:12
	<u>YU. A. DMITRIEV</u> , A. F. Ioffe Physico-Technical Institute, St. Petersburg, 194021 Russia.		

TUESDAY, JUNE 14, 1994--1:30P.M.

ROOM 100 MCPHERSON LAB

Chair: IZABEL DABROWSKI, National Research Council of Canada, Ottawa, Ontario, Canada

TH01	RYDBERG SERIES AND RYDBERG MOLECULES: AN INTRODUCTION (<i>INVITED</i>)	20 min	1:30
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GERHARD HERZBERG, Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada.

TH02	RYDBERG STATES OF THE RARE GAS DIMERS	15 min	1:52
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M. GINTER, Institute for Physical Science and Technology, University of Maryland, College Park, MD 20742.

TH03	ROTATIONAL INTERACTIONS IN THE EXCITED SINGLET UNGERADE ELECTRONIC STATES OF N ₂	10 min	2:09
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SIMON EDWARDS and LYDIA TCHANG-BRILLET, DAMAP and CNRS URA 812, Observatoire de Paris-Meudon, F-92195 Meudon Cedex, France.

TH04	RYDBERG-RYDBERG EMISSION SPECTRUM OF CARBON MONOXIDE IN THE NEAR-INFRARED REGION: AN <i>AB INITIO</i> STUDY OF NEWLY OBSERVED $^3\Pi - ^3\Sigma^+$ TRANSITION	15 min	2:21
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T. HIRANO, Department of Chemistry, Faculty of Science, Ochanomizu University, 2-1-1 Otsuka, Bunkyo-ku, Tokyo 112, Japan; K. ISHII, Department of Industrial Chemistry, Faculty of Engineering, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113, Japan; Y. SHIBA, U. NAGASHIMA, K. SATO, Department of Chemistry, Faculty of Science, Ochanomizu University, 2-1-1 Otsuka, Bunkyo-ku, Tokyo 112, Japan; and K. KAWAGUCHI, Nobeyama Radio Observatory, Minamimaki, Minamisaku, Nagano 384-13, Japan.

TH06	HIGH RESOLUTION PHOTOIONIZATION SPECTROSCOPY OF NO RYDBERG STATES	15 min	2:38
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J. GUO, A. MANK and J. W. HEPBURN, Dept. of Chemistry, University of Waterloo, Waterloo Ont., N2L 3G1, Canada.

INTERMISSION

TH07	RYDBERG STATES OF MOLECULES - AN OVERVIEW (<i>INVITED</i>)	30 min	3:15
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CHRISTIAN JUNGEN, Laboratoire Aimé Cotton du CNRS, Université de Paris-Sud, 91405 Orsay, France.

TH08	THREE-COLOR TRIPLE RESONANCE SPECTROSCOPY OF HIGHLY EXCITED ng RYDBERG STATES OF NO	15 min	3:50
	<u>A. FUJII</u> , Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980, Japan; and <u>N. MORITA</u> , Institute for Molecular Science, Myodaiji, Okazaki 444, Japan.		
TH09	ROTATIONAL ANALYSIS OF THE RYDBERG STATES ($n \geq 4$, $v=0$, 1, 2) OF CO BY TRIPLE RESONANT MULTIPHOTON SPECTROSCOPY	15 min	4:07
	<u>T. EBATA</u> , <u>M. KOMATSU</u> and <u>N. MIKAMI</u> , Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980, Japan.		
TH10	RYDBERG STATES OF B_2 BY RESONANCE ENHANCED MULTIPHOTON IONIZATION SPECTROSCOPY	15 min	4:24
	<u>RUSSELL D. JOHNSON III</u> , <u>KARL K. IRIKURA</u> and <u>JEFFREY W. HUDGENS</u> , Chemical Kinetics and Thermodynamics Division, National Institute of Standards and Technology, Gaithersburg, MD 20899.		
TH11	<i>Original abstract withdrawn - replaced by post-deadline abstract:</i> ON THE LIFETIMES OF RYDBERG STATES PROBED BY DELAYED PULSED FIELD IONIZATION	15 min	4:41
	<u>F. MERKT</u> and <u>R. N. ZARE</u> , Department of Chemistry, Stanford University, Stanford, CA 94305.		
TH12	<i>Post-deadline Abstract</i> RYDBERG STATE DYNAMICS OF ROTATING, VIBRATING H_2 AND THE JAHN-TELLER EFFECT	15 min	4:58
	<u>J. A. STEPHENS</u> and <u>C. H. GREENE</u> , Joint Institute for Laboratory Astrophysics and Department of Physics, University of Colorado, Boulder, CO 80309.		
TH13	<i>Post-deadline Abstract</i> THE 7i-6h AND 7h-6g ELECTRONIC SPECTRA OF H_2 AND THE PREDICTION OF H_2 INTER-RYDBERG EMISSION IN THE INTERSTELLAR MEDIUM	15 min	5:15
	<u>R. J. STICKLAND</u> , Department of Chemistry, University of Wales College of Cardiff, P. O. Box 912, Cardiff CF1 3TB, U.K.; <u>P. B. DAVIES</u> , Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, CB2-1EW, U.K.; <u>B. J. COTTERELL</u> , Department of Chemistry, University of Wales College of Cardiff, P. O. Box 912, Cardiff CF1 3TB, U.K.; and <u>F. J. BASTERRECHEA</u> , Facultad de Ciencias, Universidad del Pais Vasco, Departamento de Quimica Fisica, Apartado 644, 48080 Bilbao, Spain.		

WEDNESDAY, JUNE 15, 1994--8:45A.M.

AUDITORIUM HITCHCOCK HALL

Chair: RUSSELL M. PITZER, The Ohio State University, Columbus, Ohio

WA01 SPECTROSCOPY AND DYNAMICS IN HIGHLY VIBRATIONALLY EXCITED MOLECULES 40 min

F. FLEMING CRIM, Department of Chemistry, University of Wisconsin-Madison, Madison, Wisconsin 53706.

WA02 QUANTITATIVE SPECTROSCOPY WITH FOURIER TRANSFORM INSTRUMENTS 40 min

J. W. C. JOHNS, Herzberg Institute of Astrophysics, National Research Council of Canada, 100 Sussex Drive, Ottawa, Ontario K1A 0R6, Canada.

INTERMISSION

WA03 LABORATORY EVIDENCE FOR THE NATURE OF THE CARRIERS OF SOME DIFFUSE INTERSTELLAR BANDS 40 min

JOHN P. MAIER, Institute of Physical Chemistry, University of Basel, Klingelbergstrasse 80, CH-4056 Basel, Switzerland.

WA04 ELECTRONIC SPECTROSCOPY AND ELECTRONIC STRUCTURE OF THE 3d TRANSITION METAL ALUMINIDES: AlCa, AlV, AlCr, AlMn, AlCo, AlNi, AlCu, AND AlZn 40 min

MICHAEL D. MORSE, Department of Chemistry, University of Utah, Salt Lake City, UT 84112.

WEDNESDAY, JUNE 15, 1994--1:30P.M.

ROOM 1153 SMITH LAB

Chair: ALFONS WEBER, National Institute of Standards and Technology, Gaithersburg, Maryland

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| WE01 | ANALYSIS OF THE H ₂ ⁸⁰ Se HIGH RESOLUTION INFRARED SPECTRUM. EQUILIBRIUM STRUCTURE | 15 min | 1:30 |
| | <p><u>J. -M. FLAUD</u>, PH. ARCAS, C. CAMY-PEYRET, Laboratoire de Physique Moléculaire et Applications, CNRS, Université Pierre et Marie Curie, Bte 76, 4, Place Jussieu, 75230 Paris Cedex 05, France; H. BÜRGER, Anorganische Chemie, FB9, Universität-Gesamthochschule, 42097- Wuppertal, Germany; and H. WILLNER, Institut für Anorganische Chemie, Universität, 30167- Hannover, Germany.</p> | | |
| WE02 | COMPARISON OF ABSORPTION SPECTRA IN THE RANGE 2000-1700 nm WITH POWER SPECTRA OF CLASSICAL TRAJECTORIES IN MOLECULES CONTAINING CH ₂ GROUPS | 15 min | 1:47 |
| | <p>GIOVANNA LONGHI and <u>SERGIO ABBATE</u>, Dipartimento di Scienze Biomediche e Biotecnologie, Università di Brescia, via Valsabbina 19, 25123 Brescia (Italy).</p> | | |
| WE03 | THE POTENTIAL ENERGY FUNCTION OF CS ₂ DERIVED FROM ROVIBRATIONAL DATA | 10 min | 2:04 |
| | <p><u>M. KOLBUSZEWSKI</u>, P. R. BUNKER, Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6; and PER JENSEN, Physikalisches-Chemisches Institut, Justus-Liebig-Universität Giessen, Heinrich-Buff-Ring 58, D-35392, Giessen, Germany.</p> | | |
| WE04 | A MODIFIED LENNARD-JONES OSCILLATOR MODEL FOR DIATOMIC POTENTIALS | 15 min | 2:16 |
| | <p><u>PHOTOS G. HAJIGEORGIOU</u> and ROBERT J. LE ROY, Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1.</p> | | |
| WE05 | ANALYTICAL RADIAL HAMILTONIANS FOR THE X ¹ Σ ⁺ STATES OF HF AND HCl | 15 min | 2:33 |
| | <p>JOHN A. COXON, Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada B3H 4J3; and <u>PHOTOS G. HAJIGEORGIOU</u>, Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1.</p> | | |
| WE06 | METHODS AND SOME RESULTS OF STUDY OF FINE ROTATIONAL STRUCTURES OF EXCITED VIBRATIONAL STATES OF POLYATOMIC MOLECULES | 15 min | 2:50 |
| | <p><u>O. N. ULENIKOV</u>, Laboratory of Applied Spectroscopy, Physics Department, Tomsk State University, 634050 Tomsk Russia.</p> | | |

INTERMISSION

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| WE07 | SpecSim - A GUI AND COMPUTATIONAL PROGRAM FOR THE MODELLING AND FITTING OF EXPERIMENTAL SPECTRA | 15 min | 3:30 |
| | <p><u>SERGEY I. PANOV</u> and TERRY A. MILLER, Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, 120 West 18th Avenue, Columbus, Ohio 43210.</p> | | |
| WE08 | EVALUATION OF ELECTRIC AND MAGNETIC PROPERTIES OF DIATOMIC MOLECULES FROM VIBRATION-ROTATIONAL SPECTRA OF SAMPLES WITHOUT EXTERNALLY APPLIED FIELDS | 15 min | 3:47 |
| | <p><u>J. F. OGILVIE</u>, Academia Sinica, Institute of Atomic and Molecular Sciences, P. O. Box 23-166, Taipei 10764, Taiwan.</p> | | |
| WE09 | DEFINITIVE EVALUATION OF NONADIABATIC VIBRATIONAL AND ADIABATIC EFFECTS FROM VIBRATION-ROTATIONAL SPECTRA OF DIATOMIC MOLECULES | 15 min | 4:04 |
| | <p><u>J. F. OGILVIE</u>, Academia Sinica, Institute of Atomic and Molecular Sciences, P. O. Box 23-166, Taipei 10764, Taiwan.</p> | | |
| WE10 | THE USE OF TERM-VALUE FITS IN TESTING SPECTROSCOPIC ASSIGNMENTS | 15 min | 4:21 |
| | <p><u>J. K. G. WATSON</u>, Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6.</p> | | |
| WE11 | CATASTROPHES IN ROTATIONAL ENERGY SURFACES OF MOLECULES WITH INTERNAL ROTATION | 15 min | 4:38 |
| | <p><u>JUAN ORTIGOSO</u> and JON T. HOUGEN, Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, MD 20899.</p> | | |
| WE12 | ELECTRIC-FIELD INTERACTIONS IN VIBRATIONALLY HIGHLY EXCITED MOLECULES: THE $5\nu_1$ BAND OF HCCF | 15 min | 4:55 |
| | <p><u>JUAN ORTIGOSO</u>, GERALD T. FRASER, Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, MD 20899; and BROOKS H. PATE, Department of Chemistry, University of Virginia, Charlottesville, VA 22901.</p> | | |
| WE13 | <i>Post-deadline Abstract</i>
VIBRATIONAL ENERGY RELAXATION BEYOND THE GOLDEN RULE: NEW HIGH-RESOLUTION AND ULTRAFAST PERSPECTIVES | 15 min | 5:12 |
| | <p><u>R. M. BIGWOOD</u> and M. GRUEBELE, Department of Chemistry and Beckman Institute, University of Illinois, Urbana, Illinois 61801.</p> | | |
| WE14 | <i>Post-deadline Abstract</i>
THE POTENTIAL ENERGY SURFACE FOR THE ELECTRONIC GROUND STATE OF H_2^{16}O DETERMINED WITH A NEW LEVEL OF ACCURACY | 10 min | 5:29 |
| | <p>OLEG L. POLYANSKY, <u>PER JENSEN</u>, Physikalisch-Chemisches Institut, Justus Liebig-Universität Giessen, Heinrich-Buff-Ring 58, D-35392 Giessen, Germany; and JONATHAN TENNYSON, Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, United Kingdom.</p> | | |

WEDNESDAY, JUNE 15, 1994--1:30P.M.

ROOM 1009 SMITH LAB

Chair: M. CORDONNIER, University of Chicago, Chicago, Illinois

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| WF01 | LOW TEMPERATURE HELIUM PRESSURE BROADENING OF OCS, 4 - 20K | 10 min | 1:30 |
| | K. A. ROSS, K. RAMADAS, W. A. NEFF and <u>D. R. WILLEY</u> , Department of Physics, Allegheny College, Meadville PA 16335. | | |
| WF02 | THE VARIABLE TEMPERATURE PRESSURE BROADENING SPECTRUM OF CO ON HYDROGEN | 15 min | 1:42 |
| | <u>D. C. FLATIN</u> , T. M. GOYETTE and F. C. DE LUCIA, Department of Physics, The Ohio State University, 174 West 18th Avenue, Columbus, OH 43210-1106. | | |
| WF03 | THE MICROWAVE SPECTRUM AND STRUCTURE OF THE PYRIDINE...CO COMPLEX | 15 min | 1:59 |
| | <u>R. P. A. BETTENS</u> , Department of Physics, Ohio State University, Columbus, Ohio 43210; and A. BAUDER, Laboratorium für Physikalische Chemie, Eidgenössische Technische Hochschule, CH-8092 Zürich, Switzerland. | | |
| WF04 | MICROWAVE SPECTRUM AND STRUCTURE OF HF-BF ₃ | 15 min | 2:16 |
| | E. J. CAMPBELL, <u>J. A. PHILLIPS</u> , H. GOODFRIEND, A. GRUSHOW, M. CANAGARATNA, J. ALMLÖF and K. R. LEOPOLD, Department of Chemistry, University of Minnesota, Minneapolis, MN 55455. | | |
| WF05 | THE MICROWAVE SPECTRUM AND STRUCTURE OF THE METHYLACETYLENE•SO ₂ COMPLEX | 15 min | 2:33 |
| | <u>XUE-QING TAN</u> , LI-WEI XU and ROBERT L. KUCZKOWSKI, Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109-1055. | | |
| WF06 | TUNNELING MOTIONS AND METASTABLE ISOTOPOMERS IN THE MICROWAVE AND SUBMILLIMETER SPECTRA OF MIXED DEUTERATED-PROTONATED WATER DIMERS | 15 min | 2:50 |
| | E. N. KARYAKIN, Molecular Spectroscopy Laboratory, Applied Physics Institute, 46 Ulanova Street, Nizhnii Novgorod, Russia; <u>G. T. FRASER</u> , R. D. SUENRAM, F. J. LOVAS, Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, MD 20899; A. GRUSHOW, M. A. BURNS, K. R. LEOPOLD, Department of Chemistry, University of Minnesota, Minneapolis, MN 55455; and M. FUJITAKE, Department of Physics, Faculty of Science, Kanazawa University, Kanazawa, 920 Japan. | | |

INTERMISSION

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|------|---|--------|------|
| WF07 | THE ${}^{\text{Q}}\text{K}_A$ BRANCHES ($\text{K}_A \in \{2, 3, 4\}$) OF CARBODIIMIDE, HNCNH | 15 min | 3:30 |
| | <p>V. WAGENER, Physikalisch-Chemisches Institut, Justus-Liebig-Universität Giessen, Heinrich-Buff-Ring 58, D-35392 Giessen, Germany; M. BELLINI, European Laboratory for Nonlinear Spectroscopy (LENS), Largo Enrico Fermi, 2, I-50125 Florence, Italy; and M. WINNEWISSER, Physikalisch-Chemisches Institut, Justus-Liebig-Universität Giessen, Heinrich-Buff-Ring 58, D-35392 Giessen, Germany.</p> | | |
| WF08 | ROTATIONAL SPECTRA, ${}^{27}\text{Al}$ AND ${}^{14}\text{N}$ NUCLEAR QUADRUPOLE COUPLING CONSTANTS AND MOLECULAR STRUCTURE OF TRIMETHYLAMINE ALANE ($(\text{CH}_3)_3\text{NAlH}_3$) | 15 min | 3:47 |
| | <p>H. E. WARNER, Y. WANG, Department of Chemistry, Rensselaer Polytechnic Institute, Troy, NY 12180; C. WARD, Department of Physics, Cornell University, Ithaca, NY 14853; and C. W. GILLIES, Department of Chemistry, Rensselaer Polytechnic Institute, Troy, NY 12180.</p> | | |
| WF09 | MICROWAVE SPECTRUM OF $\text{CF}_3\text{CH}_2\text{OH}$ | 15 min | 4:04 |
| | <p>C. W. GILLIES, H. E. WARNER, Department of Chemistry, Rensselaer Polytechnic Institute, Troy, NY 12180; J. Z. GILLIES, Department of Chemistry, Siena College, Loudonville, NY 12221; G. FRASER, F. J. LOVAS and R. D. SUENRAM, Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, MD 20899.</p> | | |
| WF10 | THE SUBMILLIMETER-WAVE SPECTRUM OF PROPIONITRILE ($\text{C}_2\text{H}_5\text{CN}$) | 10 min | 4:21 |
| | <p>J. C. PEARSON, Department of Physics, The Ohio State University, 174 West 18th Avenue, Columbus, OH 43210-1106; K. V. L. N. SASTRY, Department of Physics, University of New Brunswick, Fredericton, New Brunswick, E3B 5A3; ERIC HERBST and FRANK C. DE LUCIA, Department of Physics, The Ohio State University, 174 West 18th Avenue, Columbus, OH 43210-1106.</p> | | |
| WF11 | THE MILLIMETER-WAVE AND SUBMILLIMETER-WAVE SPECTRUM OF PROPYLENE (CH_3CHCH_2) | 15 min | 4:33 |
| | <p>J. C. PEARSON, Department of Physics, The Ohio State University, 174 West 18th Avenue, Columbus, OH 43210-1106; K. V. L. N. SASTRY, Department of Physics, University of New Brunswick, Fredericton, New Brunswick, E3B 5A3; ERIC HERBST and FRANK C. DE LUCIA, Department of Physics, The Ohio State University, 174 West 18th Avenue, Columbus, OH 43210-1106.</p> | | |
| WF12 | THE MILLIMETER-WAVE SPECTRUM OF METHYL FORMATE (HCOOCH_3) AND SYMMETRIC DEUTERATED METHYL FORMATE (DCOOCH_3) | 15 min | 4:50 |
| | <p>L. C. OESTERLING, D. W. FERGUSON, ERIC HERBST and FRANK C. DE LUCIA, Department of Physics, The Ohio State University, 174 West 18th Avenue, Columbus, OH 43210-1106.</p> | | |

- WF13 *Post-deadline Abstract* 10 min 5:07
PRECISION BROADBAND SPECTROSCOPY IN THE TERAHERTZ REGION
- S. P. BELOV, M. LIEDTKE, G. WINNEWISSER, K. M. T. YAMADA, J. BEHREND, TH. KLAUS, R. SCHIEDER, A. H. SALECK, I. Physikalisches Institut, Universitaet zu Koeln, D-50937 Koeln, Germany; M. YU. TRETYAKOV, and A. F. KRUPNOV, Microwave Spectroscopy Laboratory, Applied Physics Institute, Nizhnii Novgorod, Russia 603024.
- WF14 *Post-deadline Abstract* 15 min 5:19
THE VARIABLE TEMPERATURE PRESSURE BROADENING SPECTRUM OF CH₃F ON HELIUM
- M. M. BEAKY, T. M. GOYETTE, and F. C. DE LUCIA, Department of Physics, The Ohio State University, 174 West 18th Avenue, Columbus, OH 43210-1106.

WEDNESDAY, JUNE 15, 1994--1:30P.M.

ROOM 1005 SMITH LAB

Chair: JAMES K. G. WATSON, National Research Council of Canada, Ottawa, Ontario, Canada

WG01 CORE-NONPENETRATING RYDBERG STATES: SPECTROSCOPIC BLACK HOLES 30 min 1:30
(INVITED)

R. W. FIELD, Z. JAKUBEK, N. HARRIS, and C. GITTINS, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139.

WG02 THE NON-PENETRATING RYDBERG STATES OF CaF 15 min 2:05

N. HARRIS, C. GITTINS and R. W. FIELD, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139.

WG03 AUTOIONIZING RYDBERG STATES OF CaCl 15 min 2:22

C. GITTINS, N. HARRIS and R. W. FIELD, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139.

WG04 BaF $v=1$ RYDBERG STATES: AUTOIONIZATION, SUPERCOMPLEXES, AND BLACK HOLES 15 min 2:39

ZYGMUNT J. JAKUBEK, Department of Chemistry, MIT, Cambridge, MA 02139; and MA HUI, Department of Modern Applied Physics, Tsinghua University, Beijing, PR China.

WG05 PULSED FIELD IONIZATION ZERO KINETIC ENERGY ELECTRON SPECTROSCOPY OF A PREDISSOCIATING STATE OF HBr^+ ($A^2\Sigma^+$) 15 min 2:56

J. D. D. MARTIN, A. MANK, T. NGUYEN and J. W. HEPBURN, Dept. of Chemistry, University of Waterloo, Waterloo Ont., N2L 3G1, Canada.

INTERMISSION

WG06 MEASUREMENTS OF EXCITED STATES IN MOLECULAR HYDROGEN TO 1 PART IN 10^8 (INVITED) 30 min 3:30

E. E. EYLER, Department of Physics and Astronomy, University of Delaware, Newark DE 19716.

WG07 LASER SPECTROSCOPIC INVESTIGATION OF HIGHER EXCITED ELECTRONIC STATES OF KAr 15 min 4:05

R. MICHALAK and D. ZIMMERMANN, Technische Universität Berlin, Institut für Strahlungs- und Kernphysik, Hardenberstr. 36, D-10623 Berlin, Germany.

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| WG08 | OBSERVATION OF RYDBERG STATES AND AUTOIONIZATION RESONANCES BY HIGH RESOLUTION ALL-OPTICAL TRIPLE RESONANCE SPECTROSCOPY | 15 min | 4:22 |
| | <u>C. C. TSAI</u> , J. T. BAHNS and W. C. STWALLEY, University of Connecticut, Department of Physics, Storrs, CT 06269. | | |
| | | | |
| WG09 | CW PFOODR SPECTROSCOPY OF TRIPLET RYDBERG AND DOUBLY EXCITED STATES OF $^7\text{Li}_2$ | 15 min | 4:39 |
| | <u>A. YIANNOPOULOU</u> , Temple University, Physics Department, Barton Hall 009-00, Philadelphia, PA 19122; B. JI, University of Connecticut, Department of Physics, Storrs, CT 06269; K. URBANSKI, LI LI, A. M. LYYRA, Temple University, Physics Department, Barton Hall 009-00, Philadelphia, PA 19122; and W. C. STWALLEY, University of Connecticut, Department of Physics, Storrs, CT 06269. | | |
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| WG10 | THE NEWLY OBSERVED $5(4S,5D) \ ^1\Delta_g$ AND $5(4S,4D) \ ^1\Pi_g$ STATES OF K_2 STUDIED BY HIGH RESOLUTION OPTICAL OPTICAL DOUBLE RESONANCE SPECTROSCOPY | 15 min | 4:56 |
| | <u>J. T. KIM</u> , H. WANG, J. T. BAHNS and W. C. STWALLEY, University of Connecticut, Department of Physics, Storrs, CT 06269. | | |

WEDNESDAY, JUNE 15, 1994--1:30P.M.

ROOM 100 MCPHERSON LAB

Chair: ERIC A. ROHLFING, Sandia National Laboratories, Livermore, California

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| WH01 | PHOTODISSOCIATION ELECTRONIC SPECTROSCOPY OF $\text{Mg}^+\text{-Rg}$ COMPLEXES | 15 min | 1:30 |
| | <u>J. S. PILGRIM</u> , C. S. YEH, K. R. BERRY and M. A. DUNCAN, Department of Chemistry, University of Georgia, Athens, Georgia 30602. | | |
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| WH02 | PHOTODISSOCIATION SPECTROSCOPY OF $\text{Mg}^+\text{-N}_2$ | 15 min | 1:47 |
| | <u>D. L. ROBBINS</u> , L. R. BROCK, J. S. PILGRIM and M. A. DUNCAN, Department of Chemistry, University of Georgia, Athens, Georgia 30602. | | |
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| WH03 | ELECTROSTATIC INTERACTIONS IN THE IONIC AND VAN DER WAALS COMPLEXES, DIRECT APPROACH | 15 min | 2:04 |
| | <u>SERGEY I. PANOV</u> and TERRY A. MILLER, Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, 120 West 18th Avenue, Columbus, Ohio 43210. | | |
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| WH04 | ROTATIONAL AND NUCLEAR HYPERFINE STRUCTURE IN THE ELECTRONIC SPECTRUM OF CuCl_2 | 15 min | 2:21 |
| | <u>M. P. BARNES</u> and J. M. BROWN, The Physical Chemistry Laboratory, University of Oxford, South Parks Road, Oxford, OX1 3QZ, UK. | | |
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| WH05 | OBSERVATION AND ANALYSIS OF THE TRIPLET-TRIPLET TRANSITION OF AlCl USING FTS | 10 min | 2:38 |
| | <u>R. J. BRETT</u> , K. I. MAHONEY and C. W. MATHEWS, Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, Columbus, OH 43210. | | |
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| WH06 | THE $\text{A } ^1\Pi - \text{X } ^1\Sigma^+$ TRANSITION OF ALUMINUM MONOBROMIDE REVISITED | 10 min | 2:50 |
| | <u>P. E. FLEMING</u> and C. W. MATHEWS, Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, Columbus, OH 43210. | | |
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| WH07 | UV SPECTROSCOPIC STUDIES OF PHOTOEXCITATION TO XeCl(B) AND XeF(B) STATES | 15 min | 3:02 |
| | E. B. GORDON, V. G. EGOROV, S. E. NALIVAICO, V. S. PAVLENKO and <u>O. S. RZHEVSKY</u> , Institute for Energy Problems of Chemical Physics, 142432, Chernogolovka, Moscow region, Russia. | | |

INTERMISSION

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| WH08 | THE SINGLET-TRIPLET TRANSITION IN H_2CSe : CASE (AB) COUPLING IN THE TRIPLET STATE OF A POLYATOMIC MOLECULE | 15 min | 3:40 |
| <p><u>DENNIS J. CLOUTHIER</u>, D. -L JOO, Department of Chemistry, University of Kentucky, Lexington, KY 40506-0055; R. H. JUDGE, Department of Chemistry, University of Wisconsin-Parkside, Kenosha WI 53141; and D. C. MOULE, Department of Chemistry, Brock University, St. Catharines, Ont., Canada L2S 3A1.</p> | | | |
| WH09 | THEORY AND APPLICATION OF THE SPIN-ROTATION HAMILTONIAN IN A CASE (A) BASIS TO THE SINGLET-TRIPLET BANDS OF SELENOFORMALDEHYDE | 10 min | 3:57 |
| <p><u>R. H. JUDGE</u>, Department of Chemistry, University of Wisconsin-Parkside, Kenosha WI 53141; <u>D. -L. JOO</u>, <u>DENNIS J. CLOUTHIER</u>, Department of Chemistry, University of Kentucky, Lexington, KY 40506-0055; and <u>D. C. MOULE</u>, Department of Chemistry, Brock University, St. Catharines, Ont., Canada L2S 3A1.</p> | | | |
| WH10 | Ni_2 REVISITED: REASSIGNMENT OF THE GROUND ELECTRONIC STATE IN AGREEMENT WITH LIGAND FIELD AND <i>AB INITIO</i> RESULTS | 15 min | 4:09 |
| <p><u>J. C. PINEGAR</u>, <u>J. D. LANGENBERG</u>, <u>C. A. ARRINGTON</u>, Department of Chemistry, University of Utah, Salt Lake City, UT 84112; <u>E. M. SPAIN</u>, Joint Institute for Laboratory Astrophysics, University of Colorado, Boulder, CO 80309; and <u>M. D. MORSE</u>, Department of Chemistry, University of Utah, Salt Lake City, UT 84112.</p> | | | |
| WH11 | PHOTODISSOCIATION MEASUREMENTS OF BOND DISSOCIATION ENERGIES: Ti_2^+ , V_2^+ , Co_2^+ , AND Co_3^+ | 15 min | 4:26 |
| <p><u>LARRY M. RUSSON</u>, Department of Chemistry, University of Utah, Salt Lake City, UT 84112; <u>SCOTT A. HEIDECKE</u>, E. I. DuPont de Nemours & Company, Textile Fibers Department, Fiber Surface Research, Kinston, NC 28502; <u>MICHELLE K. BIRKE</u>, <u>J. CONCEICAO</u>, <u>MICHAEL D. MORSE</u> and <u>P. B. ARMENTROUT</u>, Department of Chemistry, University of Utah, Salt Lake City, UT 84112.</p> | | | |
| WH12 | PHOTODISSOCIATION MEASUREMENTS OF THE BOND DISSOCIATION ENERGIES OF TiZr , TiNb , AND VZr | 10 min | 4:43 |
| <p><u>JON D. LANGENBERG</u> and <u>MICHAEL D. MORSE</u>, Department of Chemistry, University of Utah, Salt Lake City, UT 84112.</p> | | | |
| WH13 | THE $a^3\Sigma_{(u)}^+(a_1^1\Lambda_{(u)}) \rightarrow X^1\Sigma_{(g)}^+(X_0^+)$ TRANSITIONS OF GROUP VA DIMERS | 15 min | 4:55 |
| <p><u>R. BRIEDOHR</u>, <u>O. SHESTAKOV</u>, <u>K. D. SETZER</u>, <u>E. H. FINK</u>, Fachbereich Chemie, Universität Wuppertal, 42097 Wuppertal, F.R.G.; and <u>W. ZYRNICKI</u>, Institute of Inorganic Chemistry and Metallurgy of Rare Elements, Technical University of Wrocław, 50-370 Wrocław, Poland.</p> | | | |
| WH14 | ROTATION-ELECTRONIC DEPERTURBATION ANALYSIS OF THE $4f6s$ CONFIGURATIONAL STATES OF CeO | 10 min | 5:12 |
| <p><u>L. A. KALEDIN</u>, <u>J. E. McCORD</u> and <u>M. C. HEAVEN</u>, Department of Chemistry, Emory University, Atlanta, GA 30322.</p> | | | |

THURSDAY, JUNE 16, 1994--8:30P.M.

ROOM 1153 SMITH LAB

Chair: CHRISTIAN JUNGEN, Université Paris-Sud, Orsay, France

RA01	MQDT AND THE DOUBLE MINIMUM STATES OF H ₂ : BORN-OPPENHEIMER DOES NOT WORK HERE! (<i>INVITED</i>)	30 min	8:30
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STEPHEN ROSS, Department of Physics, University of New Brunswick, Fredericton, NB, Canada E3B 5A3; and CHRISTIAN JUNGEN, Laboratoire Aimé Cotton du CNRS, Université de Paris-Sud, 91405 Orsay, France.

RA02	DIFFERENCE FREQUENCY LASER SPECTROSCOPY OF THE 5g-4f RYDBERG TRANSITIONS OF H ₂	10 min	9:05
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C. UY, C. M. GABRYS and T. OKA, University of Chicago, Department of Chemistry, 5735 S. Ellis, Chicago, IL 60637-1403.

RA03	VACUUM ULTRAVIOLET FLUORESCENCE DETECTION OF TWO-PHOTON EXCITATION SPECTRA OF I ₂ RYDBERG STATES	15 min	9:17
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B. D. RAFFERTY, L. P. GOLD, and R. A. BERNHEIM, Department of Chemistry, The Pennsylvania State University, University Park, PA 16802.

RA04	THEORETICAL STUDIES OF THE RYDBERG STATE PREDISSOCIATION OF METHYL IODIDE	15 min	9:34
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H. GUO, Department of Chemistry, University of Toledo, Toledo, OH 43606; and A. H. ZEWAIL, A. A. Noyes Laboratory, California Institute of Technology, Pasadena, CA 91125.

THURSDAY, JUNE 16, 1994--10:00A.M.

ROOM 1153 SMITH LAB

Chair: TREVOR SEARS, Brookhaven National Laboratories, Upton, New York

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| RA'01 | APPLICATIONS OF TWO-COLOR RESONANT FOUR-WAVE MIXING TO SEP SPECTROSCOPY | 15 min | 10:00 |
| | J. R. DUNLOP, J. D. TOBIASON and E. A. ROHLFING, Org. 8353, MS-9055, Sandia National Laboratories, Combustion Research Facility, Livermore, CA 94551-0969. | | |
| RA'02 | SEP SPECTROSCOPY OF THE $\tilde{B}^2-A'-\tilde{X}^2A'$ SYSTEM OF JET-COOLED HCO AND DCO: VIBRATIONAL STRUCTURE OF THE \tilde{X}^2A' STATE NEAR AND ABOVE DISSOCIATION | 15 min | 10:17 |
| | J. R. DUNLOP, J. D. TOBIASON and E. A. ROHLFING, Org. 8353, MS-9055, Sandia National Laboratories, Combustion Research Facility, Livermore, CA 94551-0969. | | |
| RA'03 | TUNABLE VACUUM ULTRAVIOLET PHOFEX SPECTROSCOPY OF OCS | 15 min | 10:34 |
| | C. D. PIBEL, K. OHDE and K. YAMANOUCHI, Department of Pure and Applied Sciences, College of Arts and Sciences, The University of Tokyo, 3-8-1 Komaba, Meguro-ku, Tokyo 153 Japan. | | |
| RA'04 | SPECIFIC RATE CONSTANTS $k(E,J)$ OF NO ₂ FROM LINEWIDTH MEASUREMENTS USING OPTICAL DOUBLE-RESONANCE SPECTROSCOPY IN A FREE JET | 15 min | 10:51 |
| | B. ABEL, H. HAMANN, N. LANGE and J. TROE, Institute for Physical Chemistry, University of Goettingen, 37077 Goettingen, Germany. | | |
| RA'05 | OBSERVATION OF HIGHLY VIBRATIONALLY EXCITED $\tilde{X}^1\Sigma^+$ HCP BY STIMULATED EMISSION PUMPING SPECTROSCOPY | 15 min | 11:08 |
| | H. ISHIKAWA and R. W. FIELD, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139. | | |
| RA'06 | ANALYSIS OF THE 3 $^1A'$ STATE OF HCP | 15 min | 11:25 |
| | B. RAJARAM, J. WANG, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139; Y. T. CHEN, Department of Chemistry, National Taiwan University, Academia Sinica, Roosevelt Road, Section 4, Taipei, Taiwan 10764, Republic of China; S. L. COY and R. W. FIELD, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139. | | |
| RA'07 | THE FLUORESCENCE EXCITATION SPECTRA OF HCP AND DCP FROM 34000 CM ⁻¹ TO THE GROUND ELECTRONIC STATE DISSOCIATION THRESHOLD | 15 min | 11:42 |
| | M. A. MASON and K. K. LEHMANN, Department of Chemistry, Princeton University, Princeton, NJ 08544. | | |

RA'08 *Post-deadline Abstract*
HIGH-RESOLUTION INFRARED SPECTROSCOPY OF SrF

10 min 11:59

PINA COLARUSSO, B. GUO, K. Q. ZHANG and P. F. BERNATH, Centre for
Molecular Beams and Laser Chemistry, Department of Chemistry, University of
Waterloo, Waterloo, Ontario, Canada, N2L 3G1.

THURSDAY, JUNE 16, 1994--8:30A.M.

ROOM 1009 SMITH LAB

Chair: AGNES PERRIN, Université de Pierre et Marie Curie, Paris, France

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| RB01 | THE VIBRATIONAL ENERGY PATTERN IN PYRROLE | 15 min | 8:30 |
| | A. HELD and M. HERMAN, Laboratoire de Chimie Physique Moléculaire CPi 160/09; Université libre de Bruxelles, 50, Roosevelt ave., B-1050, Brussels, Belgium. | | |
| RB02 | DETERMINATION OF THE SPECTROSCOPIC CONSTANTS OF A DARK VIBRATIONAL STATE: FERMI AND CORIOLIS PERTURBATIONS IN THE ν_2 BAND OF FORMYL CHLORIDE | 15 min | 8:47 |
| | DENNIS J. CLOUTHIER, D. -L JOO, Department of Chemistry, University of Kentucky, Lexington, KY 40506-0055; and A. J. MERER, Department of Chemistry, The University of British Columbia, 2036 Main Mall, Vancouver, B.C., Canada V6T 1Z1. | | |
| RB03 | VIBRATIONAL OVERTONE SPECTROSCOPY OF PYRIDINE AND FLUOROPYRIDINES | 10 min | 9:04 |
| | JOYCE A. OVERLY and DEANNE SNAVELY, Center for Photochemical Sciences, Bowling Green State University, Bowling Green OH 43402. | | |
| RB04 | HIGH RESOLUTION STUDY OF THE ν_9 , ν_{10} , and ν_{11} BANDS OF CYCLOPROPANE-D ₆ | 15 min | 9:16 |
| | J. PLÍVA, Department of Physics, The Pennsylvania State University, University Park, PA 16802; A. VALENTIN and L. HENRY Laboratoire de Physique Moléculaire et Applications CNRS, Université Pierre et Marie Curie, Paris Cedex 75252, France. | | |
| RB05 | HIGH RESOLUTION INFRARED SPECTROSCOPY AND ANALYSIS OF METHYLISOCYANIDE BANDS IN THE 1370-1560 cm ⁻¹ REGION | 15 min | 9:33 |
| | L. D. LE, Department of Chemistry, The Pennsylvania State University, 152 Davey Laboratory, University Park, PA 16802; J. PLÍVA, Department of Physics, The Pennsylvania State University, 104 Davey Laboratory, University Park, PA 16802; L. P. GOLD, C. HE and R. A. BERNHEIM, Department of Chemistry, The Pennsylvania State University, 152 Davey Laboratory, University Park, PA 16802. | | |
| RB06 | RAMAN AND INFRARED SPECTRA, CONFORMATIONAL STABILITY AND <i>AB INITIO</i> CALCULATIONS OF <i>TRANS</i> -1-FLUORO-2-BUTENE | 10 min | 9:50 |
| | D. T. DURIG, Departments of Chemistry and Physics, The University of the South, Sewanee, TN 37375; MENGZHANG ZHEN, Department of Chemistry and Biochemistry, University South Carolina, Columbia, SC 29208; and J. R. DURIG, Department of Chemistry, University of Missouri-Kansas City, Kansas City, MO 64110-2499. | | |

INTERMISSION

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|------|--|--------|-------|
| RB07 | RAMAN AND INFRARED SPECTRA, CONFORMATIONAL STABILITY AND BARRIERS TO INTERNAL ROTATION OF 3-BROMO-2-METHYLPROPENE | 10 min | 10:20 |
| | <u>SAADIA ELTAYEB</u> , Department of Chemistry and Biochemistry, University South Carolina, Columbia, SC 29208; G. A. GUIRGIS and J. R. DURIG, Department of Chemistry, University of Missouri-Kansas City, Kansas City, MO 64110-2499. | | |
| RB08 | RAMAN AND INFRARED SPECTRA, CONFORMATIONAL STABILITY AND BARRIERS TO INTERNAL ROTATION OF TRIFLUOROACETYL ISOCYANATE | 10 min | 10:32 |
| | <u>K. A. KRUTULES</u> , Department of Chemistry and Biochemistry, University of South Carolina, Columbia, SC 29208; G. A. GUIRGIS and J. R. DURIG, Department of Chemistry, University of Missouri-Kansas City, Kansas City, MO 64110-2499. | | |
| RB09 | RAMAN SPECTRA AND CONFORMATIONAL STABILITY OF METHOXYDICHLOROPHOSPHINE | 10 min | 10:44 |
| | <u>J. B. ROBB, II</u> , Department of Chemistry and Biochemistry, University of South Carolina, Columbia, SC 29208; and J. R. DURIG, Department of Chemistry, University of Missouri-Kansas City, Kansas City, MO 64110-2499. | | |
| RB10 | CONFORMATIONAL STABILITY OF OXALYL CHLORIDE | 10 min | 10:56 |
| | <u>J. F. DAVIS</u> , Department of Chemistry and Biochemistry, University of South Carolina, Columbia, SC 29208; and J. R. DURIG, Department of Chemistry, University of Missouri-Kansas City, Kansas City, MO 64110-2499. | | |
| RB11 | ABSOLUTE INFRARED ABSORPTION INTENSITIES AND OPTICAL CONSTANTS OF THE NEAT LIQUIDS CH ₃ OH, CH ₃ OD, CD ₃ OH and CD ₃ OD | 15 min | 11:08 |
| | S. L. ZHANG and <u>J. E. BERTIE</u> , Department of Chemistry, University of Alberta, Edmonton, Canada, T6G 2G2. | | |
| RB12 | STEP-SCAN TIME RESOLUTION OF THE PHOTOLUMINESCENCE OF POROUS SILICON | 10 min | 11:25 |
| | <u>THOMAS J. TAGUE JR.</u> , Bruker Instruments, Inc., Fortune Drive, Manning Park, Billerica, MA 01821; GUNTHER ZACHMANN, Bruker Analytische Messtechnik GMBH, Wikingerstr. 13, Kalsruhe, Germany 76189; and MANFRED REICHE, Max Plank Institut fur Mikrostrukturphysik, Weinberg 2, Germany 06120. | | |
| RB13 | CRITICAL BEHAVIOUR OF THE ν_5 LO(177 cm ⁻¹) RAMAN MODE OF NH ₄ Br | 15 min | 11:37 |
| | <u>H. YURTSEVEN</u> , Department of Physics, Istanbul Technical University, Maslak, Istanbul-Turkey. | | |
| RB14 | SURFACE ENHANCED RAMAN SCATTERING USED AS AN <i>IN-SITU</i> ANALYTICAL METHOD FOR STUDIES OF POLYMER/METAL INTERFACE | 15 min | 11:54 |
| | GENDIN JI and <u>GI XUE</u> , Department of Chemistry, Nanjing University, The Co-ordination Chemistry State Key Laboratory, Nanjing University, Nanjing 210008, P. R. China. | | |

THURSDAY, JUNE 16, 1994--8:30A.M.

ROOM 1005 SMITH LAB

Chair: PETER BOTSCHWINA, Universität Göttingen, Göttingen, Germany

RC01 SPECTROSCOPY WITHOUT SPECTROMETER: THE ROVIBRONIC SPECTRA OF NiH, PdH, PtH (INVITED) 30 min 8:30

CHRISTEL MARIAN, Institut für Physikalische und Theoretische Chemie, Universität Bonn, Weglerstrasse 12, 53115 Bonn 1, Germany.

RC02 MOLECULAR INTEGRAL OF SPHERICAL GAUSSIAN AND ITS APPLICATION IN DIFFERENT MOLECULAR STATE GEOMETRIES 15 min 9:05

LUE-YUNG CHOW CHIU and MOHAMMAD MOHARERRZADEH, Department of Chemistry, Howard University, Washington, D.C. 20059.

RC03 ACTIVE SPACE REQUIREMENTS FOR STATE SPECIFIC MRPT AND MRAQCC METHODS 15 min 9:22

GALEN F. GAWBOY and ISAIAH SHAVITT, Department of Chemistry and The Laser Spectroscopy Facility, The Ohio State University, 120 West 18th Avenue, Columbus OH 43210.

RC04 AB INITIO COMPUTATIONS OF SEMIEMPIRICAL PI-ELECTRON METHODS: STRUCTURE AND TRANSFERABILITY OF PARAMETERS 15 min 9:39

CHARLES H. MARTIN and KARL F. FREED, The James Franck Institute and the Department of Chemistry, The University of Chicago, Chicago IL 60637.

RC05 FITS TO A NEWLY CALCULATED POTENTIAL SURFACE FOR THE REACTION $\text{Li} + \text{FH} \rightarrow \text{LiF} + \text{H}$ 15 min 9:56

P. PENDERGAST and E. F. HAYES, Department of Chemistry, The Ohio State University, Columbus OH 43210.

RC06 AB INITIO DIPOLE MOMENT SURFACE OF H_2O 15 min 10:13

G. S. KEDZIORA and I. SHAVITT, Department of Chemistry, The Ohio State University, Columbus OH 43210.

INTERMISSION

RC07 MRSD-CI STUDIES OF THE LOW LYING $^2\Delta$, $^2\Sigma$ AND $^2\Pi$ STATES OF TiN AND VC 15 min 10:50

SABA M. MATTAR, Department of Chemistry, University of New Brunswick, Bag Service No. 45222, Fredericton, New Brunswick, Canada E3B 6E2.

- RC08 ELECTRONIC STRUCTURE OF SiO: SPECTROSCOPY AND PHOTODISSOCIATION 15 min 11:07
I. DRIRA, N. FEAUTRIER, A. SPIELFIEDEL, DAMAp et URA 812 du CNRS,
Observatoire de Paris-Meudon, 5 Place J. Janssen, 92195 Meudon Principal cedex,
France.
- RC09 A THEORETICAL STUDY OF THE SPECTROSCOPY AND DYNAMICS OF STACKED
DIMERS OF AROMATIC HYDROCARBONS 15 min 11:24
R. G. SADYGOV and E. C. LIM, Department of Chemistry, University of Akron,
Akron, OH, 44325.
- RC10 ELECTRONIC STRUCTURE OF PROTACTINOCENE 10 min 11:41
KE ZHAO and RUSSELL M. PITZER, Department of Chemistry, The Ohio State
University, Columbus, OH 43210.
- RC11 *AB INITIO* CALCULATIONS FOR C₅S 10 min 11:53
S. SEEGER, J. FLÜGGE and P. BOTSCHWINA, Institut für Physikalische Chemie
der Universität Göttingen, Tammannstr.6, D-37077 Göttingen, Germany.

THURSDAY, JUNE 16, 1994--8:30A.M.

ROOM 100 MCPHERSON LAB

Chair: PRABHAKAR MISRA, Howard University, Washington D.C.

- RD01 INFRARED DIODE LASER SPECTROSCOPY OF THE ν_3 FUNDAMENTAL AND $\nu_3 + \nu_5 - \nu_5$ SEQUENCE BANDS OF THE C_4 RADICAL IN A HOLLOW CATHODE DISCHARGE 15 min 8:30

N. MOAZZEN-AHMADI, J. J. THONG, Department of Physics, University of Lethbridge, Lethbridge, Alberta T1K 3M4, Canada; and A. R. W. McKELLAR, Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6.

- RD02 THE HYPERFINE STRUCTURE OF CuCl IN ITS GROUND AND EXCITED VIBRATIONAL STATES STUDIED BY MICROWAVE FOURIER TRANSFORM (MWFT) SPECTROSCOPY 10 min 8:47

R. J. LOW, Physical Chemistry Laboratory, Oxford University, Oxford OX1 3QZ, UK; T. D. VARBERG, Department of Chemistry, Macalester College, St. Paul, Minnesota 55105; J. P. CONNELLY, Institut für Physikalische Chemie, Universität Basel, CH-4056 Basel, Switzerland; A. R. AUTY, B. J. HOWARD and J. M. BROWN, Physical Chemistry Laboratory, Oxford University, Oxford OX1 3QZ, UK.

- RD03 UV SPECTROSCOPY OF THE B^2A' AND C^2A'' STATES OF FCO 10 min 8:59

M. MATTI MARICQ, JOSEPH J. SZENTE, Research Laboratory, Ford Motor Company, P. O. Box 2053, Drop 3083, Dearborn, MI 48121; YI SU and JOSEPH S. FRANCISCO, Lab 20, Department of Chemistry, Wayne State University, Detroit, MI 48202.

- RD04 X^+ ($X = \text{Ar, Kr, N}_2$) + H_2O CHARGE-TRANSFER LUMINESCENCE: VIBRATIONALLY-SELECTED $H_2O^+ \tilde{A}-\tilde{X}$ EMISSIONS 15 min 9:11

RAINER A. DRESSLER, SUSAN T. ARNOLD, JAMES A. GARDNER, and EDMOND MURAD, Phillips Laboratory, PL/WSSI, Hanscom AFB, MA 01731-3010.

- RD05 VIBRATIONAL PREDISSOCIATION SPECTROSCOPY OF PROTONATED MOLECULES 15 min 9:28

YIBIN CAO, JONG-HO CHOI, BERND-MICHAEL HAAS and MITCHIO OKUMURA, Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, CA 91125.

- RD06 INFRARED SPECTROSCOPIC STUDIES OF $NO^+(H_2O)_n$ CLUSTERS, $n=1-5$ 15 min 9:45

JONG-HO CHOI, KEITH T. KUWATA, BERND-MICHAEL HAAS, YIBIN CAO, MATTHEW S. JOHNSON and MITCHIO OKUMURA, Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, CA 91125.

INTERMISSION

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|------|---|--------|-------|
| RD07 | GAS PHASE SOLVATION OF Na^+ WITH CH_3NH_2 : SPECTROSCOPIC AND COMPUTATIONAL RESULTS | 15 min | 10:20 |
| | <p><u>ORLANDO M. CABARCOS</u>, School of Chemical Sciences, University of Illinois at Urbana-Champaign, 505 S. Matthews Ave., Urbana, IL 61801; <u>THOMAS J. SELEGUE</u>, Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523; and <u>JAMES M. LISY</u>, School of Chemical Sciences, University of Illinois at Urbana-Champaign, 505 S. Matthews Ave., Urbana, IL 61801.</p> | | |
| RD08 | THE VIBRATIONAL STARK EFFECT AND $\text{Cs}^+(\text{NH}_3)_n$ AND $\text{Cs}^+(\text{CH}_3\text{OH})_m$ ION CLUSTERS | 15 min | 10:37 |
| | <p><u>ORLANDO M. CABARCOS</u> and <u>JAMES M. LISY</u>, School of Chemical Sciences, University of Illinois at Urbana-Champaign, 505 S. Matthews Ave., Urbana, IL 61801.</p> | | |
| RD09 | ANGULAR MOMENTUM COUPLING IN $\text{AX}(\text{?II})\text{-Rg}$ COMPLEXES | 15 min | 10:54 |
| | <p><u>W. H. BASINGER</u>, <u>U. SCHNUPF</u> and <u>M. C. HEAVEN</u>, Department of Chemistry, Emory University, Atlanta, GA 30322.</p> | | |
| RD10 | VIBRATIONAL ANALYSIS OF THE $\tilde{\text{A}} \leftarrow \tilde{\text{X}}$ TRANSITION OF $\text{Rg} \bullet \text{SH}$ COMPLEXES ($\text{Rg} = \text{Ne, Ar and Kr}$) | 15 min | 11:11 |
| | <p><u>MIN-CHIEH YANG</u>, <u>ALDO P. SALZBERG</u>, <u>CHRISTOPHER C. CARTER</u>, and <u>TERRY A. MILLER</u>, Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, 120 West 18th Avenue, Columbus, Ohio 43210.</p> | | |
| RD11 | HIGH RESOLUTION, ELECTRONIC SPECTROSCOPY OF THE RARE GAS (Ne, Ar, Kr) $\bullet \text{SH/D}$ VAN DER WAALS COMPLEXES | 15 min | 11:28 |
| | <p><u>CHRISTOPHER C. CARTER</u>, <u>JAMES M. WILLIAMSON</u> and <u>TERRY A. MILLER</u>, Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, 120 West 18th Avenue, Columbus, Ohio 43210.</p> | | |
| RD12 | HIGH RESOLUTION, ELECTRONIC SPECTROSCOPY OF RARE GAS $\bullet \text{OH/D}$ AND $\bullet \text{SH/D}$ COMPLEXES | 15 min | 11:45 |
| | <p><u>CHRISTOPHER C. CARTER</u>, Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, 120 West 18th Avenue, Columbus, Ohio 43210; <u>BOR-CHEN CHANG</u>, Chemistry Department, Brookhaven National Labs, Upton, NY 11973; <u>JAMES M. WILLIAMSON</u> and <u>TERRY A. MILLER</u>, Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, 120 West 18th Avenue, Columbus, Ohio 43210.</p> | | |
| RD13 | ELECTRONIC SPECTROSCOPY AND DYNAMICS OF THE CH/D-Ne VAN DER WAALS COMPLEXES | 15 min | 12:02 |
| | <p><u>W. H. BASINGER</u>, <u>U. SCHNUPF</u> and <u>M. C. HEAVEN</u>, Department of Chemistry, Emory University, Atlanta, GA 30322.</p> | | |

THURSDAY, JUNE 16, 1994--1:30P.M.

ROOM 1153 SMITH LAB

Chair: MARK D. MARSHALL, Amherst College, Amherst, Massachusetts

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|------|---|--------|------|
| RE01 | MICROWAVE - MILLIMETER-WAVE DOUBLE RESONANCE EXPERIMENTS ON Ar-CO | 15 min | 1:30 |
| | <u>WOLFGANG JÄGER</u> and MICHAEL C. L. GERRY, Department of Chemistry, The University of British Columbia, 2036 Main Mall, Vancouver, B.C., Canada, V6T 1Z1. | | |
| RE02 | PURE ROTATIONAL SPECTRA OF THE VAN DER WAALS DIMER Xe-CO | 15 min | 1:47 |
| | <u>KALEY A. WALKER</u> , WOLFGANG JÄGER and MICHAEL C. L. GERRY, Department of Chemistry, The University of British Columbia, 2036 Main Mall, Vancouver, B.C., Canada, V6T 1Z1. | | |
| RE03 | INFRARED SPECTRA AND ANISOTROPIC POTENTIAL ENERGY SURFACES FOR He-CO AND H ₂ -CO | 15 min | 2:04 |
| | CLAUDIO E. CHUAQUI, Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, BC V6T 1Z1, Canada; <u>ROBERT J. LE ROY</u> , Guelph-Waterloo Center for Graduate Work in Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada; and A. ROBERT W. MCKELLAR, Herzberg Institute of Astrophysics, National Research Council, 100 Sussex Drive, Ottawa, ON K1A 0R6, Canada. | | |
| RE04 | MODEL POTENTIAL FUNCTIONS FOR VAN DER WAALS TRIMERS CONTAINING CARBON DIOXIDE AND ACETYLENE | 15 min | 2:21 |
| | <u>ZHENLAN LI</u> and J. S. MUENTER, Department of Chemistry, University of Rochester, Rochester, NY 14627. | | |
| RE05 | OBSERVATION OF THE LOWEST BENDING STATE OF HeHCN BY MOLECULAR BEAM ELECTRIC RESONANCE | 15 min | 2:38 |
| | <u>S. DRUCKER</u> , F. -M. TAO and W. KLEMPERER, Department of Chemistry, Harvard University, 12 Oxford St., Cambridge, MA 02138. | | |
| RE06 | <i>AB INITIO</i> POTENTIALS AND DYNAMICS FOR He-CO, Ar-HCCH, AND Ar-HCN | 15 min | 2:55 |
| | <u>FU-MING TAO</u> , S. DRUCKER, R. COHEN and W. KLEMPERER, Department of Chemistry, Harvard University, 12 Oxford St., Cambridge, MA 02138. | | |
| RE07 | THE POTENTIAL ENERGY SURFACE OF Ne-C ₂ H ₂ FROM INFRARED SPECTROSCOPY AND THEORY | 15 min | 3:12 |
| | R. J. BEMISH and R. E. MILLER, Dept. of Chemistry, University of North Carolina, Chapel Hill, NC 27599-3290. | | |

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| RE08 | THE SPECTROSCOPY AND INTERNAL TUNNELING DYNAMICS OF THE C ₂ H ₄ -CO ₂ AND C ₂ H ₄ -N ₂ O COMPLEXES: TWO DISTINCTLY DIFFERENT SYSTEMS | 15 min | 3:45 |
| | P. A. BLOCK, WON RHEE and R. E. MILLER, Dept. of Chemistry, University of North Carolina, Chapel Hill, NC 27599-3290. | | |
| RE09 | VIBRATIONAL EIGENSTATE DETERMINATIONS: IMPROVEMENTS TO THE COLLOCATION METHOD | 15 min | 4:02 |
| | P. KORAMBATH, P. PENDERGAST, Z. DARAKJIAN and E. F. HAYES, Department of Chemistry, The Ohio State University, Columbus OH 43210. | | |
| RE10 | VIBRATIONAL COUPLINGS AND ENERGY FLOW IN COMPLEXES OF HC≡CH, HC≡CD, HC≡CC≡CH, AND N≡CH WITH NH ₃ | 15 min | 4:19 |
| | G. HILPERT, Institut für Angewandte Physik, Wegelerstr. 8, 53115 Bonn, Germany; G. T. FRASER and A. S. PINE, Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, MD 20899. | | |
| RE11 | THE SPECTROSCOPY AND DYNAMICS OF THE HF-DF AND DF-HF DIMERS: DISSOCIATION ENERGIES AND FINAL STATE DISTRIBUTIONS | 15 min | 4:36 |
| | R. J. BEMISH, MING WU, E. J. BOHAC and R. E. MILLER, Dept. of Chemistry, University of North Carolina, Chapel Hill, NC 27599-3290. | | |
| RE12 | PHOTODISSOCIATION OF ORIENTED MOLECULES: APPLICATION TO THE N ₂ -HF COMPLEX | 15 min | 4:53 |
| | R. J. BEMISH and R. E. MILLER, Dept. of Chemistry, University of North Carolina, Chapel Hill, NC 27599-3290. | | |
| RE13 | LASER-INDUCED-FLUORESCENCE DETECTION OF OVERTONE TRANSITIONS OF TWO HF CONTAINING COMPLEXES | 15 min | 5:10 |
| | S. TSANG, Department of Chemistry, Harvard University, 12 Oxford St., Cambridge, MA 02138; H. CHANG, Institute of Atomic and Molecular Science, Taipei, Taiwan, 10764, R.O.C.; R. MOLLAAGHABABA and W. KLEMPERER, Department of Chemistry, Harvard University, 12 Oxford St., Cambridge, MA 02138. | | |
| RE14 | THE BRANCHING RATIOS OF V=2 AND V=1 CHANNELS OF (HF) ₂ AND HFHCl AFTER PHOTO-DISSOCIATION | 15 min | 5:27 |
| | R. MOLLAAGHABABA, Department of Chemistry, Harvard University, 12 Oxford St., Cambridge, MA 02138; H. CHANG, Institute of Atomic and Molecular Science, Taipei, Taiwan, 10764, R.O.C.; D. D. NELSON, Aerodyne Research, Inc., 45 Manning Rd., Billerica, MA 01821; and W. KLEMPERER, Department of Chemistry, Harvard University, 12 Oxford St., Cambridge, MA 02138. | | |

THURSDAY, JUNE 16, 1994--1:30P.M.

ROOM 1009 SMITH LAB

Chair: BRUCE S. AULT, University of Cincinnati, Cincinnati, Ohio

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| RF01 | THE INFRARED SPECTRUM OF CF_3^+ TRAPPED IN SOLID NEON | 15 min | 1:30 |
| | DANIEL FORNEY and <u>MARILYN E. JACOX</u> , Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, MD 20899. | | |
| RF02 | THE INFRARED SPECTRA OF BF_2 , BF_2^+ TRAPPED IN SOLID NEON | 15 min | 1:47 |
| | <u>MARILYN E. JACOX</u> and WARREN E. THOMPSON, Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, MD 20899. | | |
| RF03 | ELECTRONIC STRUCTURE, EFFECTIVE SPIN HAMILTONIAN EXPRESSIONS, AND EXPERIMENTAL EVIDENCE FOR THE PARALLEL ELECTRON PARAMAGNETIC RESONANCES OF MATRIX-ISOLATED $(\eta^6\text{-C}_6\text{H}_6)\text{V}$ AND $(\eta^6\text{-C}_6\text{D}_6)\text{V}$ HALF-SANDWICH COMPLEXES | 15 min | 2:04 |
| | <u>SABA M. MATTAR</u> , RAMASWAMI SAMMYNAIKEN and ISRAEL UNGER, Department of Chemistry, University of New Brunswick, Bag Service No. 45222, Fredericton, New Brunswick, Canada E3B 6E2. | | |
| RF04 | ELECTRONIC AND VIBRATIONAL ABSORPTION SPECTRA OF THE TETRACENE AND PENTACENE RADICAL CATIONS ISOLATED IN ARGON MATRICES | 15 min | 2:21 |
| | <u>J. SZCZEPANSKI</u> , C. WEHLBURG, J. DRAWDY and M. VALA, Department of Chemistry, University of Florida, Gainesville, FL 32611. | | |
| RF05 | INTERNAL IONIZATION OF Ar AND Kr NOBLE-GAS CRYOCRYSTALS BY MATRIX-ISOLATED He METASTABLE EXCITED ATOMS | 15 min | 2:38 |
| | <u>R. A. ZHITNIKOV</u> and YU. A. DMITRIEV, A. F. Ioffe Physico-Technical Institute, St. Petersburg, 194021 Russia. | | |
| RF06 | INFRARED SPECTRA OF THE HYDROXYSULFONYL RADICAL HOSO_2 (THE PRECURSOR TO ACID RAIN) AND SULFURIC ACID IN SOLID ARGON AT 12 K | 15 min | 2:55 |
| | FRED PERRY, TAMMY M. JENKINS and <u>FRANK T. PROCHASKA</u> , Department of Chemistry and Physics, Western Carolina University, Cullowhee, NC 28723. | | |
| RF07 | INFRARED SPECTRUM OF S_2O_2 IN SOLID ARGON | 5 min | 3:12 |
| | <u>G. DANA BRABSON</u> and LESTER ANDREWS, Department of Chemistry, University of Virginia, Charlottesville, VA 22901. | | |

RF08	INFRARED SPECTRA OF SELENIUM OXIDES IN SOLID ARGON	15 min	3:18
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G. DANA BRABSON and LESTER ANDREWS, Department of Chemistry,
University of Virginia, Charlottesville, VA 22901.

RF09	INFRARED SPECTRA OF S_2NO AND Se_2NO IN SOLID ARGON	5 min	3:35
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G. DANA BRABSON and LESTER ANDREWS, Department of Chemistry,
University of Virginia, Charlottesville, VA 22901.

RF10	INFRARED ABSORPTION OF CIS-CIS PEROXYNITROUS ACID (HOONO) IN SOLID ARGON	15 min	3:41
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WEN-RAY LO and YUAN-PERN LEE, Department of Chemistry, National Tsing
Hua University, Hsinchu, Taiwan 30043.

THURSDAY, JUNE 16, 1994--4:15P.M.

ROOM 1009 SMITH LAB

Chair: RYAN P. A. BETTENS, The Ohio State University, Columbus, Ohio
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RF'01	THE MILLIMETER AND SUBMILLIMETER-WAVE SPECTRUM OF THE TORSIONAL STATES OF HOOH IN THE GROUND, ν_3 , AND ν_6 VIBRATIONAL STATES	15 min	4:15
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D. T. PETKIE, T. M. GOYETTE, Department of Physics, The Ohio State University, 174 West 18th Avenue, Columbus, OH 43210-1106; P. A. HELMINGER, Department of Physics, University of South Alabama, Mobile, AL 36688; and F. C. DE LUCIA, Department of Physics, The Ohio State University, 174 West 18th Avenue, Columbus, OH 43210-1106.

RF'02	THE ROTATIONAL SPECTRUM OF TRANS ETHANOL (CH ₃ CH ₂ OH)	15 min	4:32
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K. V. L. N. SASTRY, Department of Physics, University of New Brunswick, Fredericton, New Brunswick, E3B 5A3; J. C. PEARSON, M. M. BEAKY, L. C. OESTERLING, ERIC HERBST and FRANK C. DE LUCIA, Department of Physics, The Ohio State University, 174 West 18th Avenue, Columbus, OH 43210-1106.

RF'03	FT MICROWAVE CHARACTERIZATION OF THE ONION LACHRYMATOR (Z)-PROPANETHIAL S-OXIDE GENERATED BY A FLOW PYROLYSIS	15 min	4:49
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J. Z. GILLIES, Department of Chemistry, Siena College, Loudonville, NY 12211; C. W. GILLIES, H. E. WARNER and R. MALLOY, Department of Chemistry, Rensselaer Polytechnic Institute, Troy, NY 12180.

RF'04	PRECISE ROTATIONAL AND HYPERFINE PARAMETERS OF NITROSYL CHLORIDE OBTAINED USING A CAVITY PULSED MICROWAVE FOURIER TRANSFERM (MWFT) SPECTROMETER	15 min	5:06
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BETHANY GATEHOUSE, HOLGER S. P. MÜLLER, Department of Chemistry, The University of British Columbia, 2036 Main Mall, Vancouver, B.C., Canada, V6T 1Z1; NILS HEINEKING, Walther-Nerst-Institut, Humbolt-Universität zu Berlin, Berlin, Germany; and MICHAEL C. L. GERRY, Department of Chemistry, The University of British Columbia, 2036 Main Mall, Vancouver, B.C., Canada, V6T 1Z1.

RF'05	MICROWAVE FOURIER TRANSFORM SPECTROSCOPY OF SULFURYL CHLORIDE FLUORIDE, SO ₂ ClF: STRUCTURE, HYPERFINE CONSTANTS, AND HARMONIC FORCE FIELD	15 min	5:23
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HOLGER S. P. MÜLLER and MICHAEL C. L. GERRY, Department of Chemistry, The University of British Columbia, 2036 Main Mall, Vancouver, B.C., Canada, V6T 1Z1.

THURSDAY, JUNE 16, 1994--1:30P.M.

ROOM 1005 SMITH LAB

Chair: TIMOTHY G. WRIGHT, The Ohio State University, Columbus, Ohio

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| RG01 | CALCULATED SPECTROSCOPIC PROPERTIES FOR NEGATIVE MOLECULAR IONS AND CLUSTER IONS (<i>INVITED</i>) | 30 min | 1:30 |
| | <u>P. BOTSCHWINA</u> , Institut für Physikalische Chemie der Universität Göttingen, Tammannstr.6, D-37077 Göttingen, Germany. | | |
| RG02 | ACCURATE <i>AB INITIO</i> POTENTIAL SURFACES OF Ar-HF, Ar-H ₂ O, AND Ar-NH ₃ | 15 min | 2:05 |
| | <u>FU-MING TAO</u> and W. KLEMPERER, Department of Chemistry, Harvard University, 12 Oxford St., Cambridge, MA 02138. | | |
| RG03 | METALLOAROMATIC STABILIZATION OF METALLOCARBOHEDRENES | 15 min | 2:22 |
| | <u>CLINTON S. NASH</u> and BRUCE E. BURSTEN, Department of Chemistry, The Ohio State University, Columbus OH 43210. | | |
| RG04 | EXCITED POTENTIAL ENERGY SURFACES OF CH ₃ SH FROM THE <i>AB INITIO</i> EFFECTIVE VALENCE SHELL HAMILTONIAN METHOD | 15 min | 2:39 |
| | <u>JONATHAN E. STEVENS</u> , RICHARD L. GRAHAM, KARL F. FREED and MICHAEL F. ARENDT, The James Franck Institute and the Department of Chemistry, The University of Chicago, Chicago Illinois 60637. | | |
| RG05 | AB INITIO CALCULATIONS OF STRUCTURE AND VIBRATIONAL SPECTRA OF THE ALUMINUM OXIDE MOLECULES | 15 min | 2:56 |
| | <u>A. V. NEMUKHIN</u> , Department of Chemistry, Moscow State University, Moscow 119899 GSP Russia. | | |
| RG06 | HSiN: CALCULATED SPECTROSCOPIC PROPERTIES AND BARRIER HEIGHT TO ISOMERIZATION TO HSiN | 10 min | 3:13 |
| | <u>P. BOTSCHWINA</u> , M. OSWALD and E. SCHICK, Institut für Physikalische Chemie der Universität Göttingen, Tammannstr.6, D-37077 Göttingen, Germany. | | |
| RG07 | THE EQUILIBRIUM GEOMETRIES OF C ₅ AND C ₃ | 5 min | 3:25 |
| | <u>P. BOTSCHWINA</u> , Institut für Physikalische Chemie der Universität Göttingen, Tammannstr.6, D-37077 Göttingen, Germany. | | |

INTERMISSION

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| RG08 | AN <i>AB INITIO</i> CALCULATION OF THE RENNER EFFECT IN CH ₂ ⁺ | 10 min | 3:50 |
| <p>W. P. KRAEMER, Max Planck Institute of Astrophysics, Karl-Schwarzschild-Strasse 1, Postfach 1523, D-85740 Garching, Germany; PER JENSEN, Physikalisch-Chemisches Institut, Justus-Liebig-Universität Giessen, Heinrich-Buff-Ring 58, D-35392, Giessen, Germany; and P. R. BUNKER, Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6.</p> | | | |
| RG09 | VIBRATION-ROTATION SPECTRA OF H ₃ ⁺ AND ITS D ISOTOPES: A SUMMARY | 15 min | 4:02 |
| <p>J. K. G. WATSON, Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6.</p> | | | |
| RG10 | THEORETICAL ANALYSIS OF H ₃ ⁺ VIBRATIONAL STATES | 10 min | 4:19 |
| <p>NICHOLAS G. FULTON, Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, UK; GONZALO POLAVIEJA, Departamento de Química, C-IX. Universidad Autónoma de Madrid, Cantoblanco, 28049 Madrid, Spain; and JONATHAN TENNYSON, Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, UK.</p> | | | |
| RG11 | FOURFOLD CLUSTERS OF ROVIBRATIONAL ENERGIES IN H ₂ Te STUDIED WITH AN <i>AB INITIO</i> POTENTIAL ENERGY FUNCTION | 15 min | 4:31 |
| <p>PER JENSEN, Physikalisch-Chemisches Institut, Justus-Liebig-Universität Giessen, Heinrich-Buff-Ring 58, D-35392 Giessen, Germany; YAN LI, GERHARD HIRSCH, ROBERT J. BUENKER, FB 9 - Theoretische Chemie, Bergische Universität - Gesamthochschule Wuppertal, D-42097 Wuppertal, Germany; TIMOTHY J. LEE, NASA Ames Research Center, Moffett Field, California 94035; and IGOR N. KOZIN, Applied Physics Institute, Russian Academy of Science, Uljanov Street 46, 603 600 Nizhnii Novgorod, Russia.</p> | | | |
| RG12 | AN ANALYSIS OF THE TORSIONAL STRUCTURE OF ISO, TRANS AND CIS BUTENE FROM <i>AB INITIO</i> POTENTIAL SURFACES | 15 min | 4:48 |
| <p>M. L. SENENT, D. C. MOULE, and Y. G. SMEYERS, Department of Chemistry, Brock University, St. Catharines, Ontario, Canada, L2S3A1.</p> | | | |
| RG13 | <i>AB INITIO</i> STUDY OF THE ELECTRONIC SPECTRUM OF THE NCl ₂ RADICAL | 10 min | 5:05 |
| <p>Z. -L CAI, Group 325, Department of Chemistry, Nanjing University of Science and Technology, Nanjing 210014, People's Republic of China.</p> | | | |
| RG14 | METHOD FOR CALCULATING TUNNELING SPLITTING AND ISOTOPE EFFECTS IN HYDROGEN-BONDED MOLECULES | 15 min | 5:17 |
| <p>VASIL K. BABAMOV, Chemical Abstracts Service, P. O. Box 3012, Columbus OH 43210-0012.</p> | | | |

THURSDAY, JUNE 16, 1994--1:30P.M.

ROOM 100 MCPHERSON LAB

Chair: MARY-ANN H. SMITH, NASA/Langley Research Center, Hampton, Virginia

RH01 GAS-PHASE INFRARED SPECTROSCOPY OF N₂O IN A COLLISIONALLY COOLED CELL AT 5 AND 10 K 10 min 1:30

K. A. ROSS, D. R. WILLEY, Department of Physics, Allegheny College, Meadville PA 16335; A. S. MULLIN, S. SCHOWEN, L. ZHENG and G. FLYNN, Department of Chemistry and Columbia Radiation Laboratory, Columbia University, New York, NY 10027.

RH02 TUNABLE DIODE LASER SPECTROSCOPY OF CH₃F IN AN EQUILIBRIUM CELL MAINTAINED AT 7.5 KELVINS 10 min 1:42

D. R. WILLEY, K. A. ROSS, Department of Physics, Allegheny College, Meadville, PA 16335; V. DUNJKO, and A. W. MANTZ, Department of Physics and Astronomy, Franklin and Marshall College, Lancaster PA 17604-3303.

RH03 THE $\nu_2 + \nu_3$ AND $\nu_2 + \nu_3 - \nu_2$ BANDS OF NITROGEN DIOXIDE 15 min 1:54

A. PERRIN, J. -M. FLAUD, C. CAMY-PEYRET, Laboratoire de Physique Moléculaire et Applications, CNRS, Université Pierre et Marie Curie, Tour 13, bte 76, 4 Place Jussieu, F-75252 Paris, Cedex 05, France; M. HERMAN, D. HURTMANS, Laboratoire de Chimie Physique Moléculaire Cpi 160/09, Université Libre de Bruxelles, 50 Avenue F.D. Roosevelt, B-1050 Bruxelles, Belgium; and G. GUELACHVILI, Laboratoire de Physique Moléculaire et Applications, CNRS, Université Pierre et Marie Curie, Tour 13, bte 76, 4 Place Jussieu, F-75252 Paris, Cedex 05, France.

RH04 FIRST ANALYSIS OF THE $3\nu_9 - \nu_9$, $3\nu_9 - \nu_5$ AND $3\nu_9 - 2\nu_9$ BANDS OF HNO₃: TORSIONAL SPLITTING IN THE ν_9 VIBRATIONAL MODE 15 min 2:11

A. PERRIN, J. -M. FLAUD, C. CAMY-PEYRET, Laboratoire de Physique Moléculaire et Applications, CNRS, Université Pierre et Marie Curie, Tour 13, bte 76, 4 Place Jussieu, F-75252 Paris, Cedex 05, France; B. P. WINNEWISSER, S. KLEE, Physikalisches-Chemisches Institut, Justus-Liebig-Universität, D-35392 Giessen, Germany; A. GOLDMAN, F. J. MURCRAY, R. D. BLATHERWICK, F. S. BONOMO, D. G. MURCRAY, Department of Physics, University of Denver, Denver, CO 80208; and C. P. RINSLAND, NASA Langley Research Center, Atmospheric Sciences Division, Mail Stop 401A, Hampton Virginia 23681-0001.

RH05 THE MILLIMETER AND SUBMILLIMETER-WAVE SPECTRUM OF THE ν_5 AND $2\nu_9$ VIBRATIONAL STATES OF NITRIC ACID: HNO₃ 15 min 2:28

C. D. PAULSE, L. C. OESTERLING, T. M. GOYETTE, Department of Physics, The Ohio State University, 174 West 18th Avenue, Columbus, OH 43210-1106; P. A. HELMINGER, Department of Physics, University of South Alabama, Mobile, AL 36688; and F. C. DE LUCIA, Department of Physics, The Ohio State University, 174 West 18th Avenue, Columbus, OH 43210-1106.

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|---------------------|---|--------|------|
| RH06 | THE 10 μm BANDS OF THE $^{17}\text{O}_3$ ISOTOPIC SPECIES OF OZONE | 15 min | 2:45 |
| | <p>D. CONSALVO, Laboratoire de Physique des Lasers, CNRS, Université Paris XIII, Av J. -B. Clement, F-94430 Villetaneuse, France; <u>A. PERRIN</u>, J. -M. FLAUD, C. CAMY-PEYRET and A. VALENTIN, Laboratoire de Physique Moléculaire et Applications, CNRS, Université Pierre et Marie Curie, Tour 13, bte 76, 4 Place Jussieu, F-75252 Paris, Cedex 05, France.</p> | | |
| RH07 | QUASI-LINEARITY IN HCCN: THE ν_2 SPECTRUM | 15 min | 3:02 |
| | <p>W. C. ECKHOFF, C. E. MILLER and R. F. CURL, Department of Chemistry and Rice Quantum Institute, Rice University, Houston, TX 77251.</p> | | |
| INTERMISSION | | | |
| RH08 | HIGH RESOLUTION SPECTROSCOPIC STUDIES OF CH_2F_2 : THE ν_6 BAND AT 3014 CM^{-1} | 10 min | 3:40 |
| | <p>M. N. DEO, R. D'CUNHA, Spectroscopy Division, Bhabha Atomic Research Centre, Bombay 400085, India; and <u>A. WEBER</u>, Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, MD, 20899.</p> | | |
| RH09 | HIGH RESOLUTION FTIR SPECTROSCOPY OF THE ν_9 BAND OF SULFINE, H_2CSO | 10 min | 3:52 |
| | <p><u>D. -L. JOO</u>, DENNIS J. CLOUTHIER, Department of Chemistry, University of Kentucky, Lexington, KY 40506-0055; V. LAI, E. MA, C. P. CHAN and A. J. MERER, Department of Chemistry, The University of British Columbia, 2036 Main Mall, Vancouver, B.C., Canada V6T 1Z1.</p> | | |
| RH10 | FOURIER TRANSFORM EMISSION SPECTROSCOPY OF BF AND AIF | 10 min | 4:04 |
| | <p><u>K. Q. ZHANG</u>, B. GUO, Z. MORBI, F. CHARRON and P. F. BERNATH, Centre for Molecular Beams and Laser Chemistry, Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1.</p> | | |
| RH11 | OBSERVATION AND ANALYSIS OF THE HIGH RESOLUTION INFRARED EMISSION SPECTRUM OF CaF | 10 min | 4:16 |
| | <p><u>FRANÇOIS M. R. CHARRON</u>, B. GUO, K. ZHANG, Z. MORBI and P. BERNATH, Centre for Molecular Beams and Laser Chemistry, University of Waterloo, Waterloo, Ontario, Canada, N2L 3G1.</p> | | |
| RH12 | THE HIGH RESOLUTION THERMAL EMISSION SPECTRA OF InF and DF | 10 min | 4:28 |
| | <p><u>Z. MORBI</u>, T. KARKANIS, M. DULICK, J. B. WHITE, K. Q. ZHANG, F. CHARRON, B. GUO and P. BERNATH, Centre for Molecular Beams and Laser Chemistry, University of Waterloo, Waterloo, Ontario, Canada, N2L 3G1.</p> | | |
| RH13 | HIGH-RESOLUTION FT-IR EMISSION SPECTRA OF MgF AND BaF | 10 min | 4:40 |
| | <p><u>B. GUO</u>, B. BARBER, K. Q. ZHANG and P. F. BERNATH, Centre for Molecular Beams and Laser Chemistry, University of Waterloo, Waterloo, Ontario, Canada, N2L 3G1.</p> | | |

- RH14 FAR INFRARED EMISSION SPECTRA OF CsI, NaCl AND KCl 10 min 4:52
- B. GUO, V. BRAUN, R. S. RAM, G. A. McRAE, K. Q. ZHANG and P. F. BERNATH, Centre for Molecular Beams and Laser Chemistry, University of Waterloo, Waterloo, Ontario, Canada, N2L 3G1.
- RH15 TIME RESOLUTION AND FOURIER TRANSFORM SPECTROSCOPY 15 min 5:04
- G. DURRY and G. GUELACHVILI, Laboratoire de Physique Moléculaire et Applications, UPR136-CNRS, Université de Paris-sud, Bâtiment 350, 91405 Orsay, France.
- RH16 USE OF A FOURIER TRANSFORM SPECTROMETER TO STUDY ION FORMATION MECHANISMS IN A GLOW DISCHARGE 15 min 5:21
- X. HONG and TERRY A. MILLER, Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, 120 West 18th Avenue, Columbus, Ohio 43210.

FRIDAY, JUNE 17, 1994--8:30A.M.

ROOM 1153 SMITH LAB

Chair: DAVID JAMES DONALDSON, University of Toronto, Toronto, Ontario, Canada

FA01	HYPERFINE QUANTUM BEATS IN C ₂ N ₂	15 min	8:30
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N. HEMMI, J. VELAZQUEZ and T. A. COOL, School of Applied and Engineering Physics, Cornell University, Ithaca, New York 14853.

FA02	O ₂ SCHUMANN-RUNGE BAND ABSORPTION OF A STRUCTURED SOLAR SPECTRUM	15 min	8:47
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D. L. HUESTIS and T. G. SLANGER, Molecular Physics Laboratory, SRI International, Menlo Park, CA 94025.

FA03	FOURIER TRANSFORM SPECTROSCOPY OF THE HERZBERG I BANDS OF O ₂	15 min	9:04
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K. YOSHINO, J. E. MURRAY, J. R. ESMOND, W. H. PARKINSON, Harvard-Smithsonian Center for Astrophysics, 60 Garden St., Cambridge, MA 02138; A. P. THORNE and G. COX, Blackett Laboratory, Imperial College, London SW7 2BZ, UK.

FA04	LIFETIME MEASUREMENTS OF EXCITED STATES IN H ₂	15 min	9:21
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M. RAY and G. LAFYATIS, Department of Physics, The Ohio State University, Columbus OH 43210.

FA05	CRITERIA FOR COMPUTER-ASSISTED ASSIGNMENTS IN HYDROGEN EMISSION SPECTRA	15 min	9:38
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ANDREAS F. RUCKSTUHL, Seminar für Statistik, ETH-Zentrum, CH-8092 Zurich, Switzerland; and KURT DRESSLER, Physical Chemistry Lab., ETH-Zentrum, CH-8092 Zurich, Switzerland.

INTERMISSION

FA06	FLUORESCENCE SPECTROSCOPY OF ALKALI ATOMS AND ALKALI CLUSTERS ATTACHED TO LARGE LIQUID HELIUM CLUSTERS	15 min	10:15
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F. STIENKEMEIER, J. HIGGINS and G. SCOLES, Department of Chemistry, Princeton University, Princeton, NJ 08544.

FA07	LASER SPECTROSCOPY OF THE A←X TRANSITION OF LiAr	10 min	10:32
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R. BRÜHL and D. ZIMMERMANN, Technische Universität Berlin, Institut für Strahlungs- und Kernphysik, Hardenberstr. 36, D-10623 Berlin, Germany.

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| FA08 | DETERMINATION OF THE K-Ar INTERACTION POTENTIAL FOR THE X Σ AND A Π STATES FROM LASER SPECTROSCOPIC DATA | 15 min | 10:44 |
| | F. BOKELMANN and D. ZIMMERMANN, Technische Universität Berlin, Institut für Strahlungs- und Kernphysik, Hardenberstr. 36, D-10623 Berlin, Germany. | | |
| FA09 | HIGH ROVIBRATIONAL LEVELS IN THE A' Σ_u^+ AND F' Σ_g^+ STATES OF $^7\text{Li}_2$ | 15 min | 11:01 |
| | K. URBANSKI, A. YIANNPOULOU, A. M. LYYRA, Temple University, Physics Department, Barton Hall 009-00, Philadelphia, PA 19122; and LI LI, Dalian Institute of Chemical Physics, Dalian 116023, China. | | |
| FA10 | DETERMINATION OF THE LONG RANGE POTENTIAL AND DISSOCIATION ENERGY OF THE Na_2 $1^3\Delta_g$ STATE | 15 min | 11:18 |
| | B. JI, C. -C. TSAI, University of Connecticut, Department of Physics, Storrs, CT 06269; LI LI, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China; T. -J. WHANG, Department of Chemistry, National Cheng Kung University, Tainan 70101, Taiwan; H. WANG, University of Connecticut, Department of Physics, Storrs, CT 06269; A. M. LYYRA, Temple University, Physics Department, Barton Hall 009-00, Philadelphia, PA 19122; J. T. BAHNS and W. C. STWALLEY, University of Connecticut, Department of Physics, Storrs, CT 06269. | | |
| FA11 | LIGHT COLLECTION OPTICS FOR EMISSION SPECTROSCOPY ON THE BRUKER IFS 120 HR SPECTROMETER | 10 min | 11:35 |
| | P. E. FLEMING, K. I. MAHONEY and C. W. MATHEWS, Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, Columbus, OH 43210. | | |
| FA12 | REANALYSIS OF VIBRATIONAL RESONANCES IN SiH_2 $\tilde{X}^1\text{A}_1$ | 10 min | 11:47 |
| | H. ISHIKAWA, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139; and O. KAJIMOTO, Department of Chemistry, Kyoto University, Kyoto, Japan, 606-01. | | |
| FA13 | CHARACTERIZATION OF THE INTERACTING (1) $^3\Pi_g$ AND (2) $^3\Pi_g$ STATES OF THE B_2 MOLECULE | 15 min | 11:59 |
| | C. R. BRAZIER and P. G. CARRICK, Phillips Laboratory/RKFE, Edwards AFB, CA 93524-7680. | | |
| FA14 | FOURIER TRANSFORM EMISSION SPECTRUM OF THE TRIPLET SYSTEM OF BH | 10 min | 12:16 |
| | C. R. BRAZIER, Phillips Laboratory/RKFE, Edwards AFB, CA 93524-7680. | | |
| FA15 | <i>Post-deadline Abstract</i>
OXYGEN OPTICAL TRANSITION IN COLLISION COMPLEX WITH CHLORINE ATOM | 5 min | 12:28 |
| | VITALINA V. KUKUEVA and BORIS F. MINAEV, Cherkassy Engineering and Technological Institute, Cherkassy, 257006, Ukraine. | | |

FRIDAY, JUNE 17, 1994-8:30A.M.

ROOM 1009 SMITH LAB

Chair: JEAN-MARIE FLAUD, Université de Pierre et Marie Curie, Paris, France

FB01	THE VIBRATIONAL ENERGY PATTERN IN ACETYLENE I	15 min	8:30
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M. ABBOUTI TEMSAMANI, Laboratoire de Chimie Physique Moléculaire CPi 160/09; Université libre de Bruxelles, 50, Roosevelt ave., B-1050, Brussels, Belgium; Q. KOU, G. GUELACHVILI, Laboratoire de Physique Moléculaire et Applications, Université de Paris-Sud, Orsay Cédex 91405, France; A. PISARCHIK, The Institute of Physics of the Academy of Sciences of Belarus Scarina ave., 70, 220602, Minsk, Belarus; A. HELD and M. HERMAN, Laboratoire de Chimie Physique Moléculaire CPi 160/09; Université libre de Bruxelles, 50, Roosevelt ave., B-1050, Brussels, Belgium.

FB02	THE VIBRATIONAL ENERGY PATTERN IN ACETYLENE II	10 min	8:47
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M. ABBOUTI TEMSAMANI and M. HERMAN, Laboratoire de Chimie Physique Moléculaire CPi 160/09; Université libre de Bruxelles, 50, Roosevelt ave., B-1050, Brussels, Belgium.

FB03	INTRAMOLECULAR VIBRATIONAL REDISTRIBUTION IN SEVERAL OVERTONE BANDS OF DIACETYLENE AND DIACETYLENE-D ₁	15 min	8:59
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J. E. GAMBOGI, R. Z. PEARSON, Department of Chemistry, Princeton University, Princeton, NJ 08544; X. YANG, Department of Chemistry, UC Berkeley, Berkeley, CA 94720; K. K. LEHMANN and G. SCOLES, Department of Chemistry, Princeton University, Princeton, NJ 08544.

FB04	PRECISION MEASUREMENTS OF ACETYLENE SPECTRA AT 1.4-1.7 μ m RECORDED WITH 16-352m PATHLENGTH	15 min	9:16
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KAREN A. KEPPLER, K. NARAHARI RAO, Department of Physics, The Ohio State University, Columbus, OH 43210-1106; JOSEF PLÍVA, Department of Physics, The Pennsylvania State University, University Park, PA 16802; STEFAN KLEE, GEORG MELLAU, BRENDA P. WINNEWISSER and MANFRED WINNEWISSER, Physikalisch-Chemisches Institut, Justus-Liebig-Universität Giessen, D-35392 Giessen, Germany.

FB05	MOLECULAR DYNAMICS IN ACETYLENE: EFFECTIVE HAMILTONIAN MODELS AND OPTIMAL INTERMEDIATE STATES FOR DISPERSED FLUORESCENCE SPECTRA	15 min	9:33
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S. A. B. SOLINA, J. P. O'BRIEN, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139; W. POLIK, Department of Chemistry, Hope College, Holland, MI 49423; and R. W. FIELD, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139.

FB06 THE VIBRATIONAL ENERGY PATTERN IN N₂O 10 min 9:50

M. BACH, D. HURTMANS, A. HELD, J. VANDER AUWERA and M. HERMAN,
Laboratoire de Chimie Physique Moléculaire CPi 160/09; Université libre de
Bruxelles, 50, Roosevelt ave., B-1050, Brussels, Belgium.

INTERMISSION

FB07 THE VIBRATIONAL ENERGY PATTERN IN N₂O₄ 5 min 10:20

Y. ELYOUSSOUFI, Laboratoire de Chimie Physique Moléculaire CPi 160/09;
Université libre de Bruxelles, 50, Roosevelt ave., B-1050, Brussels, Belgium; I.
KLEINER, Laboratoire de Physique Moléculaire et Applications, Université Pierre et
Marie Curie et C.N.R.S., Tour 14, 4, Place Jussieu, 75252 Paris Cédex 05, France;
M. HERMAN and J. LIEVIN, Laboratoire de Chimie Physique Moléculaire CPi
160/09; Université libre de Bruxelles, 50, Roosevelt ave., B-1050, Brussels, Belgium.

FB08 REINVESTIGATION OF THE 2ν₁ BAND IN TRIFLUOROPROPYNE USING 15 min 10:26
INFRARED/INFRARED DOUBLE RESONANCE

M. BECUCCI, Laboratorio Europeo di Spettroscopia Non-lineari (LENS), Largo E.
Fermi No. 2 (Arcetri), 50125 Firenze, Italy; J. E. GAMBOGI, K. K. LEHMANN and
G. SCOLES, Department of Chemistry, Princeton University, Princeton, NJ 08544.

FB09 ANALYSIS OF THE 2ν₃ BAND OF CF₄ (2540-2600 cm⁻¹) 15 min 10:43

A. NIKITIN, T. GABARD, J. P. CHAMPION, G. PIERRE, Laboratoire de
Physique, Université de Bourgogne, Equip associée au C.N.R.S., 6 Boulevard
Gabriel, 21000 Dijon, France; A. G. ROBIETTE, Computing Service, Oxford
University, 13 Banbury Road, Oxford OX2 6NN, UK; and A. S. PINE, Molecular
Physics Division, National Institute of Standards and Technology, Gaithersburg, MD
20899.

FB10 THE HIGH RESOLUTION IR SPECTRUM OF SEVERAL BANDS OF t-¹³CHF=¹³CHF: THE 15 min 11:00
MOLECULAR STRUCTURE OF t-1,2-DIFLUOROETHYLENE

NORMAN C. CRAIG, OLIVER P. ABI OG, BAONIAN HU, Department of
Chemistry, Oberlin College, Oberlin, OH 44074; and W. J. LAFFERTY, Molecular
Physics Division, NIST, Gaithersburg, MD 20899.

FB11 FOURIER TRANSFORM SPECTROSCOPY AND FIR LASER EMISSION IN THE CH₃- 15 min 11:17
ROCKING BAND OF C-13 METHANOL

A. PREDOI, CEMAID and Physics Department, University of New Brunswick,
Fredericton, N.B., Canada E3B 5A3; LI-HONG XU, Molecular Physics Division,
National Institute of Standards and Technology, Gaithersburg, Maryland 20899; R. M.
LEES, CEMAID and Physics Department, University of New Brunswick, Fredericton,
N.B., Canada E3B 5A3; M. NOEL, and J. W. C. JOHNS, Herzberg Institute of
Astrophysics, N.R.C., Ottawa, Ont., Canada K1A 0R6.

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| FB12 | ABSOLUTE INTENSITY MEASUREMENTS IN $^{16}\text{O}^{12}\text{C}^{32}\text{S}$: THE $\nu_1 + \nu_3$ REGION | 10 min | 11:34 |
| | Q. ERRERA, J. VANDER AUWERA and A. FAYT, Laboratoire de Spectroscopie Moléculaire-Université Catholique de Louvain-Chemin du cyclotron 2-1348 Louvain-La-Neuve-Belgium. | | |
| FB13 | <i>Post-deadline Abstract</i>
A ROVIBRATIONAL ANALYSIS OF THE ν_2 C-H STRETCHING VIBRATION ENERGY MANIFOLD IN THE LINEAR SPECIES HCN-HF | 15 min | 11:46 |
| | A. M. GALLEGOS, A. L. MCINTOSH, J. W. BEVAN, Department of Chemistry, Texas A&M University, College Station, Texas 77840. | | |
| FB14 | <i>Post-deadline Abstract</i>
INVESTIGATION OF THE GROUND VIBRATIONAL STATE STRUCTURE OF H^{35}Cl TRIMER BASED ON RESOLVED K , J SUBSTRUCTURE OF THE ν_5 VIBRATIONAL BAND | 15 min | 12:03 |
| | J. HAN, Z. WANG, A. L. MCINTOSH, R. L. LUCCHESI and J. W. BEVAN, Department of Chemistry, Texas A&M University, College Station, Texas 77840. | | |
| FB15 | <i>Post-deadline Abstract</i>
ROVIBRATIONALLY RESOLVED, CONTINUOUS SUPERSONIC-JET FOURIER-TRANSFORM, INFRARED ABSORPTION SPECTROSCOPY OF WEAKLY BOUND DIMERS | 15 min | 12:20 |
| | R. MEADS, Department of Chemistry, M.I.T., Cambridge, Massachusetts 02139; C. HARTZ, R. LUCCHESI and J. BEVAN, Department of Chemistry, Texas A&M University, College Station, Texas 77840. | | |
| FB16 | <i>Post-deadline Abstract</i>
DIODE LASER SPECTROSCOPY IN A $\text{N}_2 - \text{H}_2 - \text{He}$ DISCHARGE: THE ν_4 BAND OF NH_3^+ | 15 min | 12:37 |
| | FRANK KÜHNEMANN, SANGWOO JOO and TAKESHI OKA, Department of Chemistry and Department of Astronomy and Astrophysics, The University of Chicago, Chicago, Illinois 60637-1403. | | |
| FB17 | <i>Post-deadline Abstract</i>
DISCHARGE MODULATION TECHNIQUE IN A SUPERSONIC JET FOR INFRARED DIODE LASER ABSORPTION SPECTROSCOPY | 10 min | 12:54 |
| | TAKASHI IMAJO, KEIICHI TANAKA and TAKEHIKO TANAKA, Department of Chemistry, Faculty of Science, Kyushu University 33, Hakozaki, Higashiku, Fukuoka 812, Japan. | | |

FRIDAY, JUNE 17, 1994--8:30A.M.

ROOM 1005 SMITH LAB

Chair: FRANK J. LOVAS, National Institute of Standards and Technology, Gaithersburg, Maryland

FC01 THE MICROWAVE SPECTRUM OF THE OPEN-SHELL COMPLEX ArNO_2 15 min 8:30

R. J. LOW, C. J. WHITHAM, Physical Chemistry Laboratory, Oxford University, Oxford, OX1 3QZ, UK; T. D. VARBERG, Department of Chemistry, Macalester College, St. Paul, Minnesota 55105; and B. J. HOWARD, Physical Chemistry Laboratory, Oxford University, Oxford, OX1 3QZ, UK.

FC02 DETERMINATION OF THE STRUCTURE OF HBr OCS 15 min 8:47

A. R. HIGHT WALKER, WEI CHEN, STEWART E. NOVICK, Department of Chemistry, Wesleyan University, Middletown, CT 06459; BRIAN D. BEAN and MARK D. MARSHALL, Department of Chemistry, Amherst College, Amherst, MA 01002.

FC03 DIPOLE MOMENT OF THE LOWEST II BENDING STATE OF $(\text{HCN})_2$ 15 min 9:04

A. GRUSHOW, W. A. BURNS and K. R. LEOPOLD, Department of Chemistry, University of Minnesota, Minneapolis, MN 55455.

FC04 PROTON INTERCHANGE TUNNELING AND FREE INTERNAL ROTATION IN $\text{H}_3\text{N--HSH}$ 15 min 9:21

G. HILPERT, Institut für Angewandte Physik, Wegelerstr. 8, 53115 Bonn, Germany; E. N. KARYAKIN, Molecular Spectroscopy Laboratory, Applied Physics Institute, 46 Ulanova Street, Nizhnii Novgorod, Russia; G. T. FRASER and R. D. SUENRAM, Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, MD 20899.

FC05 INFRARED SPECTROSCOPY OF THE C-O STRETCHING BAND IN METHANOL/ACETONE DIMER 10 min 9:38

W. D. STORK, C. T. LAUSH and J. M. LISY, Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801.

FC06 GLOBAL FIT OF TUNNELING SPLITTINGS IN THE $K=0$ A-TYPE MICROWAVE SPECTRUM OF THE METHANOL DIMER 15 min 9:50

NOBUKIMI OHASHI, Department of Physics, Faculty of Science, Kanazawa University, Kakuma, Kanazawa, Japan 920-11; and JON T. HOUGEN, Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, MD 20899.

INTERMISSION

FC07 PATTERNS OF ORIENTATIONAL ORDER IN POLAR CLUSTERS 15 min 10:30

HOLLY B. LAVENDER, KARTHIK A. IYER and SHERWIN J. SINGER, Department of Chemistry, Ohio State University, Columbus, OH 43210.

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|------|---|--------|-------|
| FC08 | DETECTION OF NON-RADIATIVE RELAXATION CHANNELS IN ELECTRONICALLY EXCITED MOLECULES USING OPTOTHERMAL DETECTION | 10 min | 10:47 |
| | <u>C. CAMERON MILLER</u> , KEVIN B. HEWETT and LAURA A. PHILIPS,
Department of Chemistry, Cornell University, Ithaca, NY 14853. | | |
| FC09 | HIGH RESOLUTION INFRARED SPECTROSCOPY OF PYRAZINE AND NAPHTHALENE IN A MOLECULAR BEAM | 15 min | 10:59 |
| | <u>KEVIN B. HEWETT</u> , MEIHUA SHEN, CHRISTOPHER L. BRUMMEL and
LAURA A. PHILIPS, Department of Chemistry, Cornell University, Ithaca, NY 14853. | | |
| FC10 | 10 μ m INFRARED SPECTRUM OF TETRAHYDROFURAN: QUENCHING OF CORIOLIS INTERACTIONS IN THE VIBRATIONALLY EXCITED STATE | 10 min | 11:16 |
| | <u>ANNE M. ANDREWS</u> , Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, MD 20899; BROOKS H. PATE, Department of Chemistry, University of Virginia, Charlottesville, VA 22901; C. CAMERON MILLER, Department of Chemistry, Cornell University, Ithaca, NY 14853; ADRIAN AINETSCHIAN, Abteilung Chemische Physik, Universität Ulm, D-89069 Ulm, Germany; and GERALD T. FRASER, Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, MD 20899. | | |
| FC11 | MICROWAVE MEASUREMENTS OF THE $V=0 \rightarrow 1$ AND $V=2 \rightarrow 3$ PSEUDOROTATION BANDS OF TETRAHYDROFURAN | 10 min | 11:28 |
| | <u>ANNE M. ANDREWS</u> , Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, MD 20899; BROOKS H. PATE, Department of Chemistry, University of Virginia, Charlottesville, VA 22901; and GERALD T. FRASER, Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, MD 20899. | | |
| FC12 | HIGH RESOLUTION INFRARED STUDY OF <i>GAUCHE</i> -1,1,2-TRIFLUOROETHANE: INTRAMOLECULAR INTERACTIONS AND VIBRATIONAL MODE COUPLING | 10 min | 11:40 |
| | <u>SASHA G. ALCOTT</u> , C. CAMERON MILLER, STEPHEN C. STONE and LAURA A. PHILIPS, Department of Chemistry, Cornell University, Ithaca, NY 14853. | | |
| FC13 | INFRARED-MICROWAVE DOUBLE RESONANCE SPECTROSCOPY OF THE C-F STRETCHING FUNDAMENTAL AND TWO PERTURBING STATES OF 2-FLUOROETHANOL | 15 min | 11:52 |
| | <u>ANNE M. ANDREWS</u> , Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, MD 20899; BROOKS H. PATE, Department of Chemistry, University of Virginia, Charlottesville, VA 22901; C. CAMERON MILLER, LAURA A. PHILIPS, Department of Chemistry, Cornell University, Ithaca, NY 14853; and GERALD T. FRASER, Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, MD 20899. | | |
| FC14 | AN INFRARED DOUBLE RESONANCE STUDY OF PROPYNE BY PUMPING THE WEAK $\nu_3 + 2\nu_9$ BAND | 10 min | 12:09 |
| | <u>THOMAS CRONIN</u> , JUNGSUG GO and DAVID S. PERRY, Department of Chemistry, The University of Akron, Akron, OH 44325-3601. | | |

- FC15 *Post-deadline Abstract* 15 min 12:21
A STUDY OF THE $\text{Pb}(^3\text{P}_0) + \text{O}_2(^1\Delta_g)$ REACTION WITH ULTRAVIOLET PHOTOELECTRON SPECTROSCOPY

DARREN HAGGERSTON and JOHN M. DYKE, Department of Chemistry, The University, Southampton, S09 5NH, United Kingdom.

- FC16 *Post-deadline Abstract* 15 min 12:38
INFRARED LASER SPECTROSCOPY OF THE LINEAR C_{13} CARBON CLUSTER

T. F. GIESEN, A. VAN ORDEN, H. J. HWANG, R. S. FELLERS, R. A. PROVENÇAL, and R. J. SAYKALLY, Department of Chemistry, University of California, Berkeley, CA, 94720.

- FC17 *Post-deadline Abstract* 15 min 12:55
THE FAR INFRARED SPECTRUM OF $(\text{NH}_3)_2$ BETWEEN 80 AND 100 cm^{-1}

J. G. LOESER, J. D. CRUZAN, E. BITTEN, M. BROWN, and R. J. SAYKALLY, Department of Chemistry, University of California, Berkeley, CA, 94720.

FRIDAY, JUNE 17, 1994--8:30A.M.

ROOM 100 MCPHERSON LAB

Chair: CHRISTEL MARIAN, Universität Bonn, Bonn, Germany

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| FD01 | <i>AB INITIO</i> CALCULATION OF THE VIBRATIONAL STRUCTURE OF PHOTOELECTRON SPECTRA FOR FREE RADICALS | 15 min | 8:30 |
| | M. HORN and P. BOTSCHWINA, Institut für Physikalische Chemie der Universität Göttingen, Tammannstr.6, D-37077 Göttingen, Germany. | | |
| FD02 | VIBRATIONAL FREQUENCIES, IONIZATION ENERGIES AND HEATS OF FORMATION OF METHYL-SUBSTITUTED AMIDOGEN RADICALS | 15 min | 8:47 |
| | TIMOTHY G. WRIGHT and TERRY A. MILLER, Laser Spectroscopy Facility, Chemistry Department, The Ohio State University, Columbus, Ohio 43210. | | |
| FD03 | POTENTIAL ENERGY SURFACES FOR OH($X^2\Pi$, $A^2\Sigma^+$) + RARE GAS OPEN SHELL VAN DER WAALS COMPLEXES: HOW WELL CAN <i>AB INITIO</i> THEORY PREDICT THEM? | 15 min | 9:04 |
| | U. SCHNUPF, M. C. HEAVEN, D. G. MUSAIEV and K. MOROKUMA, Department of Chemistry, Emory University, Atlanta, GA 30322. | | |
| FD04 | <i>AB INITIO</i> CALCULATION OF THE CH($X^2\Pi$, $A^2\Delta$, $B^2\Sigma^-$, $C^2\Sigma^+$) + Ne (1S) POTENTIAL ENERGY SURFACES | 15 min | 9:21 |
| | U. SCHNUPF, M. C. HEAVEN, D. G. MUSAIEV and K. MOROKUMA, Department of Chemistry, Emory University, Atlanta, GA 30322. | | |
| FD05 | COMPARATIVE <i>AB INITIO</i> STUDY OF BENDING POTENTIALS FOR MgNC AND CaNC | 15 min | 9:38 |
| | KEISAKU ISHII, Department of Industrial Chemistry, Faculty of Engineering, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113, Japan; TSUNEO HIRANO, Department of Chemistry, Faculty of Science, Ochanomizu University, 2-1-1 Otsuka, Bunkyo-ku, Tokyo 112, Japan; and KOICHI YAMASHITA, Institute for Fundamental Chemistry, Takano-Nishihiraki-cho, Sakyo-ku, Kyoto 606, Japan. | | |
| FD06 | A THEORETICAL INVESTIGATION OF THE CH ₂ CN AND CH ₂ NC RADICALS | 10 min | 9:55 |
| | R. OSWALD and P. BOTSCHWINA, Institut für Physikalische Chemie der Universität Göttingen, Tammannstr.6, D-37077 Göttingen, Germany. | | |
| FD07 | THE EQUILIBRIUM STRUCTURE AND WAVENUMBERS OF TOTALLY SYMMETRIC VIBRATIONS FOR H ₂ CCCC CALCULATED <i>AB INITIO</i> | 5 min | 10:07 |
| | P. BOTSCHWINA and M. OSWALD, Institut für Physikalische Chemie der Universität Göttingen, Tammannstr.6, D-37077 Göttingen, Germany. | | |

FRIDAY, JUNE 17, 1994--10:30A.M.

ROOM 100 MCPHERSON LAB

Chair: KAREN ANN KEPLER, The Ohio State University, Columbus, Ohio

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|-------|---|--------|-------|
| FD'01 | RADIOFREQUENCY/OPTICAL DOUBLE RESONANCE SPECTROSCOPY OF He ₂ | 15 min | 10:30 |
| | ANNE NOERREGAARD, IRENE HAZELL and <u>NIS BJERRE</u> , Institute of Physics and Astronomy, Aarhus University, DK-8000 Aarhus C. Denmark. | | |
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| FD'02 | DEVELOPMENT OF A PULSED MOLECULAR BEAM FOURIER TRANSFORM MICROWAVE SPECTROMETER IN THE 26 TO 40 GHz REGION | 15 min | 10:47 |
| | I. MERKE, Laboratoire de Physique Moléculaire et Applications, Bat. 350, Université de Paris-Sud, F-91405 Orsay Cedex, France; H. DREIZLER and <u>W. STAHL</u> , Institut für Physikalische Chemie der Universität Kiel, 24098 Kiel, Germany. | | |
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| FD'03 | A MILLIMETER-WAVE STUDY OF THE HCCCS AND DCCCS RADICALS | 15 min | 11:04 |
| | <u>M. C. MCCARTHY</u> , J. M. VRTILEK, E. W. GOTTLIEB, F. -M. TAO, Harvard University, Department of Chemistry, Harvard University, Cambridge, MA 02138; C. A. GOTTLIEB and P. THADDEUS, Harvard University, Division of Applied Sciences, Cambridge, MA 02138. | | |
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| FD'04 | POINT DEFECT ACTIVITY IN AMORPHOUS SOLID WATER AND THE POSSIBLE ROLE OF DEFECT ACTIVITY IN THE GLASS TRANSITION | 15 min | 11:21 |
| | <u>M. FISHER</u> and J. P. DEVLIN, Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma 74075. | | |
| | | | |
| FD'05 | ANHARMONICITY OF THE VIBRATIONS OF SiC ₂ AND Si ₂ C AT 2000 K | 15 min | 11:38 |
| | <u>R. W. SCHMUDE, JR.</u> and K. A. GINGERICH, Department of Chemistry, Texas A&M University, College Station TX 77843. | | |
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| FD'06 | SELECTIVE LASER SPECTROSCOPY OF MOLECULAR IONS UO ₂ ²⁺ ADSORBED ON DISPERSED SiO ₂ SURFACE | 10 min | 11:55 |
| | <u>Yu. D. GLINKA</u> , Institute of Surface Chemistry of the Ukrainian Academy of Sciences, Nauka ave. 31, 252650 Kiev, Ukraine; and T. B. KRAK, Department of Physics, Kiev State University, Acad. Glushkov ave. 6, 252127 Kiev, Ukraine. | | |
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| FD'07 | THE ABSORPTION SPECTRA OF THE Cu(II) BETA-DIKETONATE VAPOURS IN THE 115-300 nm REGION | 15 min | 12:07 |
| | E. F. REZNIKOVA, V. P. NAZ'MOV and <u>I. K. IGUMENOV</u> , Institute of Inorganic Chemistry of the Siberian Division of the Russian Academy Sciences, 630090 Novosibirsk, Russia. | | |

FD'08	SPECTROSCOPIC EVIDENCE FOR HYDROGEN MIGRATION IN HALO-CYCLOHEXADIENYL RADICALS IN SOLID ARGON	15 min	12:24
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P. HASSANZADEH and J. H. MILLER, Department of Chemistry, The George Washington University, Washington DC 20052.

FD'09	THE NATURAL ABSORPTION OF AQUAPHILOUS CRYSTAL SEMICONDUCTORS	15 min	12:41
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N. P. NETESOVA, Department of Physics, Lomonosov State University of Moscow, Russia.

MA01**40 min**

NEW INTERSTELLAR MOLECULES

P. THADDEUS

Since 1968 interstellar and circumstellar molecules have been discovered at an average rate of nearly 4 per year, and there is no indication at the present time that the rate of discovery is flagging. New very powerful millimeter-wave and submillimeter radio telescopes and interferometers, supported by laboratory investigations of greater and greater sensitivity and sophistication—especially spectroscopic studies of exotic molecules such as radicals, ions, carbon chains, isomers, and carbenes—have largely been responsible for this continuing progress. Some of the astronomical facilities and new techniques will be described, and a sample of recent astronomical and laboratory discoveries presented. Linear carbon chains continue to be a dominant structural theme in interstellar chemistry, and recent discoveries include highly unfamiliar carbon chain radicals, carbenes, isomers, and chains with terminal metal atoms.

Address: Division of Applied Sciences and Center for Astrophysics, Harvard University, Cambridge MA 02138

MA02**40 min**

Large Amplitude Motions of Molecules
and Ions Revealed by Supersonic Jet Spectroscopy

Mitsuo Ito
Institute for Molecular Science
Okazaki, Japan

Several laser electronic spectroscopies are applied for the study of large amplitude motions of aromatic molecules and ions in supersonic jets. The internal rotation of the CH₃ group in substituted toluenes in ground, excited and ionic states is mainly discussed. Large-amplitude "butterfly tunneling" motion in 1,2,4,5-tetrafluorobenzene is also described.

INTERMISSION

<p><i>PRESENTATION OF 1993 RAO PRIZE AWARDS</i></p>
<p><i>Jennifer M. Campbell, University of Waterloo</i></p> <p><i>Hao Li, Cornell University</i></p> <p><i>J. Bradley White, University of Waterloo</i></p>

MA03

40 min

Electronic Spectra of Semiconductor Nanocrystals

A. Paul Alivisatos

Department of Chemistry
University of California
Berkeley, CA 94720

ABSTRACT

In recent years, techniques have been developed to prepare highly monodisperse and crystalline particles of many common semiconductors in the nanometer size regime. These particles, consisting of a hundred to tens of thousands of atoms, exhibit electronic spectra that evolve in interesting ways with size. Recent experiments on electric field modulation of absorption and emission, resonance Raman scattering and photon echoes will be presented, with a view towards presenting a unified picture of the electronic spectra in these materials.

ME01 15 min 1:30

THE COLLISION-INDUCED FUNDAMENTAL BAND OF NITROGEN AT LOW TEMPERATURES

W.B. Olson, W.J. Lafferty, A. Weber and A.M. Solodov

A minimum-astigmatism multiple-reflection absorption cell, which matches the aperture of the NIST BOMEM Model DA3 FT spectrometer, has been designed and constructed. The cell has a base length of 2 meters and is designed to be chemically inert. It can be used over pressures up to 12 atm and to temperatures down to -45°C , with optical path lengths up to 116 m. The optical system is substantially temperature independent. Conditions for minimum astigmatism will be discussed.

This cell has been used to study the collision induced spectrum of the $v=1-0$ band of N_2 gas around 2320 cm^{-1} at a path length of 84 m with pressures up to 12 atm at 6 temperatures over the range 228 to 296 K with a resolution of 0.1 cm^{-1} . Absorbance at any point in the band is found to be proportional to the square of the gas density. The band profile is in good agreement with previous studies, but small features on the P-, Q- and R-branches, previously noted at much lower temperatures and attributed to dimeric species^{1,2}, are also seen in our spectra. The total integrated absorption coefficient for the band is $3.467(6) \times 10^{-4}\text{ cm}^{-2}\text{ Amagat}^{-2}$ at 293 K, and a very small temperature dependence of this coefficient has been observed.

1. C.A. Long, G. Henderson, and G.E. Ewing, Chem. Phys. **2**, 485 (1973).
2. A.R.W. McKellar, J. Chem. Phys. **88**, 4190 (1988)

Address of Olson: 348 North Summit Ave., Gaithersburg, MD 20877

Address of Lafferty and Weber: Molecular Physics Division, NIST, Gaithersburg, MD 20899

Address of Solodov: Institute of Atmospheric Optics, 1 Akademicheskij Ave., 634055 Tomsk, Russia

ME02 15 min 1:47

THE OVERTONE TRANSITIONS OF $^{12}\text{C}^{16}\text{O}_2$ AND $^{13}\text{C}^{16}\text{O}_2$ IN THE NEAR INFRARED

X. Yang and C. Noda

The vibrational overtone transitions of gaseous $^{12}\text{C}^{16}\text{O}_2$ and $^{13}\text{C}^{16}\text{O}_2$ were observed by using the photoacoustic technique in the spectral range of $11000 - 14000\text{ cm}^{-1}$. The recorded transitions for both $^{12}\text{C}^{16}\text{O}_2$ [1] and $^{13}\text{C}^{16}\text{O}_2$ are (00051 - 00001), (10051 - 00001) and (10052 - 00001). By comparing the integrated band intensities of water in the same spectral range to that of the $5\nu_3$ transition of $^{12}\text{C}^{16}\text{O}_2$ and from the knowledge of absorption intensities of water, the absolute absorption intensities of the $5\nu_3$ band of $^{12}\text{C}^{16}\text{O}_2$ was determined. The intensities of the other transitions were obtained by comparing the integrated band intensities to that of the $5\nu_3$ band of $^{12}\text{C}^{16}\text{O}_2$. It was found that the intensity of the (10051 - 00001) transition is comparable to that of the (00051 - 00001) transition.

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- [1]. A. Adel and D. M. Dennison, Phys. Rev. **43**, 716 (1933)

Address of Yang and Noda: Department of Chemistry, University of New Hampshire, Durham, NH 03824 USA

ME03 15 min 2:04

PRESSURE BROADENING AND SPIN SPLITTINGS IN THE ν_3 -BAND OF NO_2

B. SUMPF, V.V. PUSTOGOV, P. HEINTGES, F. KÜHNEMANN, H.-D. KRONFELDT

We present experimental results for the determination of broadening coefficients and spin splittings in the ν_3 band of NO_2 obtained with a Tunable Diode Laser Spectrometer using pulse driven diode lasers. We investigated altogether 39 lines with $16 \leq N'' \leq 48$ and $0 \leq K_a'' \leq 12$ in the P branch of NO_2 near 1572 cm^{-1} . The collisional broadening was measured using NO_2 , N_2 , He, Kr, and Ar as perturbers. Using fit techniques it was possible to determine individual broadening coefficients for all the lines under study and spin splittings of the measured doublet components. For the broadening coefficients we obtain the tendency $\gamma_{\text{NO}_2-\text{Ar}} > \gamma_{\text{NO}_2-\text{He}} > \gamma_{\text{NO}_2-\text{Kr}}$ in the case of noble gas broadening. The broadening coefficients were measured as a function of the quantum numbers N'' and K_a'' for all the perturbers. There is no definite tendency in the K_a'' dependence, but the difference between the broadening coefficients are larger than the experimental uncertainty.

The nitrogen broadening coefficient was measured, too. There was no clear decrease or increase of the values with N'' or K_a'' , so that we calculated an averaged nitrogen broadening coefficient $\gamma_{\text{NO}_2-\text{N}_2} = (0.070 \pm 0.011) \text{ cm}^{-1}/\text{atm}$. The values of the spin-splittings are in good agreement with theoretical values from A. Perrin.

Address of Sumpf, Pustogov, Heintges and Kronfeldt

Optisches Institut der Technischen Universität Berlin, Sekr. PN 0-1
Hardenbergstraße 36, 10623 Berlin, Germany

present Address of Kühnemann

University of Chicago, Dept. of Chemistry,
5735 S. Ellis Avenue, Chicago/IL 60637, USA

ME04 15 min 2:21

H_2O LINE POSITION MEASUREMENTS AT 1000K

M.P. ESPLIN, R.B. WATTSON, AND M.L. HOKE

A 20 torr H_2O sample has been heated to 1000K in a 1.75 m stainless steel absorption cell and the spectrum measured with a Michelson interferometer using a maximum optical path difference of 114 cm resulting in an apodized resolution of 0.009 cm^{-1} . More than 1200 lines were identified in the 1000 to 1400 cm^{-1} spectral region. A Loomis-Wood diagram technique proved extremely useful in making the line assignments. After a number of lines had been identified, knowledge of the energy levels derived from these identified lines was used to identify additional lines in a boot-strapping process. When the observed line positions were compared to the line positions on the HITRAN 92 data base¹, discrepancies of up to 0.8 cm^{-1} were found. An important source of self-consistent spectral line data used with the Loomis-Wood diagram technique was obtained from a DND (direct numerical diagonalization) calculation². These line positions were calculated using a 47-parameter potential surface with up to hexic powers in internal coordinates and generated with a consistent nonlinear least-squares fit. The results of the analysis and comparisons with other researchers will be presented at the symposium.

This work was supported by the Air Force Office of Scientific Research (AFOSR) as part of PL/GL Task 2310G1.

1. L.S. Rothman et al, *JQSRT* **48**, 469 (1992).

2. R.B. Wattson and L.S. Rothman, *JQSRT* **48**, 763 (1992).

Address of Esplin and Wattson: Stewart Radiance Laboratory, Utah State University, 139 The Great Road, Bedford, Ma 01730.

Address of Hoke: Geophysics Directorate,
Phillips Laboratory/GPOS, 29 Randolph Road, Hanscom AFB, Bedford, MA 01731.

ME05 10 min 2:38

Characterization of Candidate DIAL Lidar Water Vapor Absorption Lines in the Two micron Region, Michael E. Thomas, Raymond M. Sova, David Tobin, Daniel Byrum and L. Larrabee Strow

DIAL lidar for water vapor remote sensing in the eye safe 2 μm region has been receiving much interest. Such systems rely on accurate spectral line characterization. Typically the HITRAN data base on atmospheric spectral lines is used. A series of transmittance measurements are made to verify and improve the HITRAN data base in this important spectral region.

A 3 meter base path White cell attached to a BOMEM DA3.02 is used for the transmittance measurements. The White cell is set to a path length of 216 meters for all experiments. Measurements of pure water at various pressures and nitrogen broadened water vapor are collected at room temperature. Data analysis is performed on lines that are relatively temperature insensitive over the range of typical atmospheric temperatures and lines that are accessible by lasers. The measured spectrum is converted to the absorption coefficient and is fitted to a synthetic spectrum to determine the spectral line parameters. Some lines show good agreement (within a few percent) with the HITRAN database, other lines disagree by more than $\pm 10\%$. Thus care must be exercised in applying the HITRAN data based to DIAL lidar applications.

Address of Thomas and Sova, The Johns Hopkins University, Applied Physics Laboratory, Laurel, Maryland 20723.

Address of Tobin, Byrum and Strow, Department of Physics, University of Maryland Baltimore County, Baltimore Maryland 21228.

ME06 15 min 2:50

SHIFTS OF H_2O SPECTRAL LINES IN $\nu_1 + 3\nu_3$ VIBRATIONAL BAND INDUCED BY THE PRESSURE OF NOBLE GASES, A.D. Bykov, V.V. Lazarev, Yu.N. Ponomarev, V.N. Stroinoval, and B.A. Tikhomirov

The H_2O absorption lines shifts induced by pressure of noble gases like He, Ne, Ar, Kr, and Xe were investigated in the visible spectral range near 0.7 μm using the dual-channel photoacoustic laser spectrometer with the spectral resolution of 0.01 cm^{-1} . The measurements of the shifts of the vibration-rotation lines of $\nu_1 + 3\nu_3$ band were made at several buffer gas pressures inside the interval from 100 to 760 torr.

The experimental values of shift coefficients were compared with the theoretical ones. The method of calculations is described in details including the trajectories curvature effect of the colliding molecules. In the case of H_2O molecule collisions with He and Ne atoms the best agreement between experimental and theoretical data is observed when the curvature of trajectories of colliding partners is taken into account. The problem of optimal determining of polarizability of H_2O molecule in excited vibrational state is also discussed.

Address of Bykov, Lazarev, Ponomarev, Stroinoval, and Tikhomirov: Institute of Atmospheric Optics, SB Russian Sci. Acad., Tomsk, 634055, Russia.

INTERMISSION

ME07 10 min 3:30

TEMPERATURE DEPENDENCE OF AIR-BROADENING AND SHIFT COEFFICIENTS OF O₃ LINES IN THE ν_1 BAND

M. A. H. SMITH, V. MALATHY DEVI, D. CHRIS BENNER, AND C. P. RINSLAND

We have recorded high-resolution absorption spectra of ozone broadened by dry air at a number of temperatures from -63°C to 23°C using the Fourier transform spectrometer at the McMath-Pierce facility of the National Solar Observatory on Kitt Peak. The spectra cover the 600-2700 cm⁻¹ region at 0.005 cm⁻¹ resolution. Broadening gas pressures varied from approximately 100 to 250 Torr. Using a multispectrum nonlinear least-squares procedure^{1,2}, we fit 29 of these spectra simultaneously to determine the air-broadening and shift coefficients and their temperature dependences for nearly 550 lines in the ν_1 band. Self-broadening coefficients were also determined. These results cover a wide range of rotational quantum numbers, particularly in the *R* branch, with $J'' \leq 55$ and $K_a'' \leq 12$. The variation of the retrieved broadening and shift parameters with the rotational quantum numbers has been examined; particularly interesting behavior is noted as the value of K_a'' approaches that of J'' .

The broadening and shift results compare well with previous room-temperature measurements in the ν_1 band, and they are also consistent (within the stated uncertainties) with the few previous measurements of the temperature dependence of air-, N₂- and O₂-broadening coefficients in other O₃ bands. Results in the ν_2 band have recently been obtained (see the following paper), and analysis of lines in the $\nu_1 + \nu_3$ band is in progress.

1. D. Chris Benner, C. P. Rinsland, V. Malathy Devi, and M. A. H. Smith, 48th Ohio State University International Symposium on Molecular Spectroscopy, ME11, June 14, 1993.
2. V. Malathy Devi, D. Chris Benner, M. A. H. Smith, and C. P. Rinsland, JQSRT, in press (1994).

Address of Smith and Rinsland: Atmospheric Sciences Division, NASA Langley Research Center, Mail Stop 401A, Hampton, VA 23681-0001

Address of Malathy Devi and Benner: Department of Physics, The College of William and Mary, Williamsburg, VA 23187-8795

ME08 10 min 3:42

TEMPERATURE DEPENDENCE OF AIR-BROADENING AND SHIFT COEFFICIENTS OF ¹⁶O₃ LINES IN THE ν_2 BAND

V. MALATHY DEVI, D. CHRIS BENNER, M. A. H. SMITH, AND C. P. RINSLAND

We have recorded a large number of high-resolution (0.005 cm⁻¹) absorption spectra in the 600-2700 cm⁻¹ region of O₃ (generated using a natural isotopic sample of oxygen) broadened by dry air. These spectra were obtained at various temperatures between -63 and 23°C using the McMath-Pierce Fourier transform spectrometer at the National Solar Observatory on Kitt Peak. Using a multispectrum^{1,2} nonlinear least-squares procedure a total of 29 spectra were analyzed simultaneously to determine the broadening and shift coefficients and their temperature dependences for more than 400 transitions in the ν_2 fundamental of ¹⁶O₃. Variation of the broadening and shift coefficients with the rotational quantum numbers within the ν_2 band will be discussed. These results will be compared with the values determined for the same parameters in the ν_1 band of ¹⁶O₃.

1. D. Chris Benner, C. P. Rinsland, V. Malathy Devi, and M. A. H. Smith, 48th Ohio State University International Symposium on Molecular Spectroscopy, ME11, June 14, 1993.
2. V. Malathy Devi, D. Chris Benner, M. A. H. Smith, and C. P. Rinsland, JQSRT, in press (1994).

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ME09**15 min****3:54****PRESSURE BROADENING IN THE ν_1 and ν_3 BAND OF SO_2** **COLLISIONS WITH SO_2 , N_2 , AIR, He, Ne, Kr, Ar, Xe****B. SUMPE, O. FLEISCHMANN, Y. HEINER, J. WASCHULL, I. MEUSEL, H.-D. KRONFELDT**

We present recent experimental results on self-, air and noble gas broadening in the ν_1 and ν_3 band of SO_2 , obtained with a Tunable Diode Laser Spectrometer with pulse driven lasers. Our investigations cover the spectral region between 1073 cm^{-1} and 1148 cm^{-1} for the ν_1 band and the region between 1321 cm^{-1} and 1367 cm^{-1} for the ν_3 band. For both bands we had investigated mostly lines of the P branch. We determine the broadening coefficient for collisions with SO_2 , N_2 , air, He, Ne, Kr, Ar and in some cases Xe for 31 lines with $3 \leq J'' \leq 44$ and $0 \leq K_a'' \leq 19$ in the ν_1 band and 23 lines from three selected wave number regions with $4 \leq J'' \leq 62$ and $0 \leq K_a'' \leq 23$ in the ν_3 band.

Using several types of fit algorithms (non linear least squares fit, blind search, evolution strategy) we achieve an experimental uncertainty of 5%. First evaluations in the ν_1 band shows for the noble gas broadening the tendency $\gamma_{\text{SO}_2-\text{Kr}} > \gamma_{\text{SO}_2-\text{Ar}} > \gamma_{\text{SO}_2-\text{He}} > \gamma_{\text{SO}_2-\text{Ne}}$. The analysis of the data in the ν_3 band is in progress.

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Y. H. and J. W. wish to thank the Deutsche Bundesstiftung Umwelt for a grant

ME10**15 min****4:11****LINESHAPE ASYMMETRIES IN Ar-BROADENED $\text{HF}(\nu=1-0)$ IN THE DICKE-NARROWING REGIME,****A.S. PINE**

Collisional lineshapes have been measured for the fundamental band transitions of HF in an Ar buffer gas at $T=296(1) \text{ K}$ using a tunable difference-frequency laser spectrometer. The broadening and shift coefficients are in excellent agreement with recent close-coupling scattering cross section calculations (S. Green and J. Hutson, J. Chem. Phys. 100, 891 (1994)) based on a realistic intermolecular potential surface determined by high-resolution infrared and microwave spectroscopy of the Ar-HF van der Waals complex. At pressures below 1 bar, the lineshapes exhibit strong collisional (Dicke) narrowing of the Doppler distribution and a slight asymmetry which we model with hard collision (Rautian) or soft collision (Galatry) profiles modified for partial correlation between velocity- and state-changing collisions.

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ME11 15 min 4:28
AN EMPIRICAL EXPRESSION FOR LINE WIDTHS OF AMMONIA FROM FAR-INFRARED MEASUREMENTS, L. R. BROWN AND D. B. PETERSON

The hydrogen-broadened line widths of $116 \text{ }^{14}\text{NH}_3$ ground state transitions between $J,K = 1,0$ to $10,10$ have been measured at 0.006 cm^{-1} resolution using a Bruker spectrometer in the 40 to 210 cm^{-1} region. These experimental data have been fitted to $\pm 3\%$ using an heuristically derived expression of the form

$$\gamma = a_0 + a_1 J + a_2 K + a_3 J^2 + a_4 JK$$

where J and K are the lower state symmetric top quantum numbers. This function has also been applied to widths of 58 transitions near $3 \text{ }\mu\text{m}$ reported by Pine et al. [J. Mol. Spectrosc. **50**, 337-348, 1992]. The percent differences between the observed and calculated widths are 5% or better for five foreign broadeners (N_2 , O_2 , Ar, H_2 , and He). For the self-broadening, the expression fails to reproduce the $K=0$ data, and the rms rises to 11%.

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ME12 15 min 4:45
LINE MIXING IN THE ν_3 BAND OF METHANE, D. CHRIS BENNER, V. MALATHY DEVI, MARY ANN H. SMITH AND CURTIS P. RINSLAND

The ν_3 band of methane is important for studies of the Earth's atmosphere both because of its strength (so that small amounts of methane can be detected remotely) and due to its interference in the detection of other gases such as HCl which absorb in the same spectral region. The P and R branch manifolds in this band are more compact than other strong methane bands and the effects of line mixing are apparent. The effects of line mixing are, however, difficult to sort out from Lorentz broadening and line shifts when analyzing laboratory spectra. With our multispectrum nonlinear least squares fitting technique these effects are better separated from one another. Improved characterization of this band using spectra from interferometers of the National Solar Observatory and the Université de Paris-Sud has been attained for air and self broadening. The results require that there be either mixing between lines of different species (A, E or F) or else between manifolds (which are about 10 cm^{-1} apart.)

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ME13 15 min 5:02

PRESSURE BROADENING OF LARGER MOLECULES - THE ν_{14} -BAND OF C_6H_6

B. SUMPF, J. WASCHULL, Y. HEINER, I. MEUSEL, F. KÜHNEMANN, V.V. PUSTOGOV, H.-D. KRONFELDT

We present first results on the pressure broadening in the ν_{14} band of C_6H_6 , i.e. we investigated collisions of C_6H_6 with C_6H_6 and air near 1024.6 cm^{-1} and 1050.2 cm^{-1} . Using autocorrelation technique for the determination of an averaged broadening coefficient we found a self broadening coefficient of $(0.13 \pm 0.01)\text{ cm}^{-1}/\text{atm}$ and an air broadening coefficient of $(0.086 \pm 0.025)\text{ cm}^{-1}/\text{atm}$ for the 1024.6 cm^{-1} region (PP branch, $37 \leq J'' \leq 43$). In the region near 1050.2 cm^{-1} (RR branch, $30 \leq J'' \leq 38$) the air broadening coefficient is remarkably larger $(0.139 \pm 0.001)\text{ cm}^{-1}/\text{atm}$ and even larger than the self broadening coefficient stated above.

Additional we will present first results for individual line parameters using a fit algorithm.

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ME14 10 min 5:19

CALCULATION OF ROTATIONAL STATE-TO-STATE OZONE RELAXATION RATES FOR O_3 - N_2 , O_3 - O_2 AND O_3 - O_3 COLLISIONS AND MODELIZATION OF THE $(100) \leftrightarrow (001)$ CORIOLIS-ASSISTED INTERMODE TRANSFER, F. MENARD-BOURCIN, C. BOURSIER, C. BOULET, L. DOYENNETTE, J. MENARD AND J.-M. FLAUD

Rotational state-to-state rate constants have been calculated for O_3 -M collisions ($M = O_3, N_2, O_2$) by a semi-classical method based on multipolar and atom-atom potentials. Calculations lead to a strong propensity for first-order quadrupolar transitions when the perturber is diatomic and to a propensity for both first-order quadrupolar- and dipolar-type transitions for self relaxation.

The $(100) \leftrightarrow (001)$ Coriolis-assisted intermode transfer, observed when pumping O_3 molecules in a (100) rotational state and monitoring the ensuing population increase in a (001) rotational state, is too fast to be a pure near-resonant vibrational-vibrational energy transfer but results mainly from successive rotational energy transfers within the $(100,001)$ dyad. We have then developed a kinetic model describing, by means of the calculated state-to-state rates, the rotational energy transfers within a large set of $(100,001)$ rotational states. Such a kinetic model simulates as well pure rotational energy transfers as rovibrational transfers. It was applied to the available experimental data.

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MF01 15 min 1:30

EXTENSION OF THE ABSORPTION PATH LENGTH IN A CRYOGENIC SAMPLE: THE INFRARED SPECTRUM OF SOLID H_2 MEASURED WITH PATH LENGTHS OF 3.8, 15, AND 33 cm

R. A. STEINHOFF, B. P. WINNEWISSER, M. WINNEWISSER, and K. NARAHARI RAO

Two sets of experiments have been carried out in an attempt to increase the absorption path in a cryogenic sample, the size of which is limited to 3 or 4 cm by the dimensions of commonly used dewars. The first development was the construction of a small White-type cell using thin film technology ^a. New features in the spectrum of solid hydrogen obtained with that system have been reported ^b. The second development is the use of two on-axis spherical mirrors to delimit the sample and reflect the infrared beam up to seven times through the crystal. This contribution reports the results obtained with the latter optical arrangement. The optical system will be described and the spectra obtained for solid hydrogen presented.

^aR. Steinhoff, K. V. S. R. Apparao, D. W. Ferguson, K. Narahari Rao, B. P. Winnewisser, and M. Winnewisser *Appl. Optics* **32**, 6577-6581 (1993)

^bR. Steinhoff, K. V. S. R. Apparao, D. W. Ferguson, K. Narahari Rao, B. P. Winnewisser, and M. Winnewisser *Can. J. Phys.*, in press

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MF02 20 min 1:47

CONDON MODULATION SPECTROSCOPY OF SOLID HYDROGEN

KAREN E. KERR, DAVID P. WELIKY, TAKAMASA MOMOSE, ROBERT M. DICKSON, and TAKESHI OKA

The Condon effect,¹ in which an electric field induces otherwise forbidden transitions, has recently been used to induce and modulate the $Q_1(0)$ vibrational fundamental of solid parahydrogen.^{2,3} Condon modulation has resulted in a two order of magnitude improvement in the sensitivity of solid hydrogen spectroscopy and has allowed the observation of Raman type transitions in the infrared. The linewidth and line position of the field induced $Q_1(0)$ transition has been studied as a function of temperature and orthohydrogen concentration. The line shift has been explained as resulting from the temperature variation of the molar volume and thus the intermolecular distances.

The enhanced sensitivity of Condon modulation has been exploited in the observation of the $Q_3(0)$ overtone of parahydrogen and has been applied to the $Q_1(0)$ and $Q_1(1)$ transitions of deuterium impurities in parahydrogen. Several of the features in the field modulated $Q_1(0)$ D_2 impurity spectrum which are induced by the much larger quadrupolar fields of $J=1$ orthohydrogen and paradeuterium appear to be Stark shifted.

1. E. U. Condon. *Phys. Rev.*, **41**, 759(1932).

2. K. E. Kerr, T. Momose, C. M. Gabrys, D. P. Weliky, and T. Oka. 48th International Symposium on Molecular Spectroscopy. Columbus, Ohio. June 1993. Paper **RE08**.

3. K. E. Kerr, T. Momose, D. P. Weliky, C. M. Gabrys, and T. Oka. *Phys. Rev. Lett.*, submitted.

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Address of Momose: Department of Chemistry, Faculty of Science, Kyoto University, Kyoto 606-01, Japan

MF03 15 min 2:09

EXTENDED OBSERVATION AND COMPREHENSIVE ASSIGNMENT OF THE $Q_1(0)$ VIBRATIONAL SPECTRA OF D_2 AND HD IMPURITIES IN SOLID PARAHYDROGEN

DAVID P. WELIKY, KAREN E. KERR, TERESA J. BYERS, YU ZHANG, AND TAKESHI OKA

Greater spectrometer sensitivity has allowed us to observe new transitions in the $Q_1(0)$ vibrational spectra of impurity D_2 and HD in solid parahydrogen^{1,2}. Because of these more comprehensive spectra and our greater theoretical understanding, we have been able to completely assign the observed transitions. The resulting energy level diagrams for the different impurities give a precise description of $J=1/J=0$ impurity pair interactions in the solid.

One interesting discovery is the large variation of line broadening between different $Q_1(0)$ transitions. This is qualitatively explained with a quadrupolar broadening mechanism.

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1. M. C. Chan, L. W. Xu, C. M. Gabrys, and T. Oka, *J. Chem. Phys.* **95**, 9494 (1991).
 2. D. P. Weliky, K. E. Kerr, T. Momose, T. J. Byers, and T. Oka, Columbus 1992, Paper RG02.
-

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MF04 15 min 2:26

OBSERVATION AND ANALYSIS OF THE $Q_3(0)$ TRANSITION OF SOLID PARAHYDROGEN

Robert M. Dickson, Takamasa Momose, Teresa J. Byers, Karen E. Kerr, and Takeshi Oka

The second overtone of the pure vibrational transition of solid parahydrogen has been observed at 0.85 μm under high resolution with a continuous wave titanium sapphire laser. Although similar to the D_2 and HD impurity results in a parahydrogen host matrix, the transition of the host molecule exhibits different symmetries, and therefore splittings, in the ground and excited states due to a change in quantization axis. As a result, the splitting patterns and polarization dependencies for the parahydrogenic $Q_3(0)$ ($v=3 \leftarrow 0$, $J=0 \leftarrow 0$) transition are very different from those of the impurity Q transitions. Due to the interaction of the $J=1$ molecule inducing the transition with the absorbing $J=0$ hydrogen, an interesting progression in splitting patterns from the fundamental to the second vibrational overtone is observed.

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MF05 20 min 2:43
OBSERVATION OF THE $S_3(0)$ TRANSITION IN SOLID PARAHYDROGEN AND THE DEVELOPMENT OF A THEORY OF $\Delta J=2$ ROVIBRATIONAL LINEWIDTHS.

Robert M. Dickson and Takeshi Oka

The $S_3(0)$ transition ($v=3 \leftarrow 0$, $J=2 \leftarrow 0$) in solid para-hydrogen has been observed at $12058.982 \text{ cm}^{-1}$ with a width of 0.252 cm^{-1} (FWHM). The linewidth of this transition is broader than that of the pure rotational $S_0(0)$ transition. Although linewidths usually narrow with vibrational excitation due to a larger phonon-excitation energy discrepancy and diminished coupling among molecules, all observed $S_v(0)$ ($v=v \leftarrow 0$, $J=2 \leftarrow 0$, for $v=1, 2, 3$) transitions exhibit linewidths which are larger than that of the pure rotational transition. The $S_v(0)$ linewidths are shown to be a result of the mixing of the simultaneous state $Q_v(0) + S_0(0)$ manifold ($v=v \leftarrow 0$, $J=0 \leftarrow 0$ and $v=0 \leftarrow 0$, $J=2 \leftarrow 0$, respectively, for two neighboring molecules) into the zeroth order $S_v(0)$ manifold. The linewidths of all $S_v(0)$ transitions are reproduced theoretically by considering the consequences of simultaneously placing two excitons, $Q_v(0)$ and $S_0(0)$, in the lattice. By considering the roton's dephasing due to the presence of the simultaneously-created $Q_v(0)$ excitation, one can calculate the contribution of this coherence relaxation (i.e. T_2 relaxation) process to the overall frequency uncertainty of each $S_v(0)$ transition.

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INTERMISSION

MF06 15 min 3:20
Multiphonon Absorption in Diamond, Michael E. Thomas

Diamond is a purely covalent material with no fundamental infrared active vibrational modes. Intrinsic diamond is completely transparent below the band gap except for two-, three- and higher-order multiphonon absorption bands located in the mid-IR. Results on experimental measurements of infrared transmittance on Type IIa and CVD diamond as a function of temperature are presented. The measurements show the first observation of the four-phonon band in diamond and the two-phonon red wing out to 900 cm^{-1} . Diamond absorbance near 1000 cm^{-1} is of particular interest because many infrared sensors operate at this atmospheric window.

Multiphonon absorption band models have been successfully developed for ionic materials. This is the first application of such a model on a purely covalent material. To obtain a fit to the experimental data, the phonon density of states function required considerable modification relative to other ionic materials studied. Evidence indicates that the absorption in this region is caused by two-phonon acoustic-acoustic interactions. In most materials, pure acoustic multiphonon absorption usually is not measurable because it is obscured by strong one-phonon optical mode absorption. Diamond has very high acoustic frequencies owing to its strong bonds, and the lack of fundamental absorption unmasks the pure acoustic contribution. This acoustic contribution is modeled by applying a Debye acoustic phonon density of states distribution function. Good agreement with room temperature experimental data is obtained.

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MF07 15 min 3:37

EXPERIMENTAL AND SIMULATED SPECTRA OF ICE SURFACES, BARE AND WITH ADSORBATES: ASSIGNMENT OF SURFACE-LOCALIZED MODES, B. ROWLAND, J. P. DEVLIN, AND N.S. KADAGATHUR

A new method of making ice samples with large surface areas by depositing nanocrystals of ice on an IR transparent window, has increased the intensity of surface-defect modes, and has greatly improved signal to noise levels. This allows a comprehensive look at the IR adsorption of surface molecules by eliminating bulk-ice bands. Difference spectra are used to eliminate overlapping bulk-ice bands in the following ways: difference spectra between a) two spectra of the same sample at the same temperature with the only difference being the amount of annealing of each spectrum and b) bare surface spectra and adsorbate saturated surface spectra at the same temperature, showing adsorbate-shift of surface-defect modes. A useful simulated difference spectrum is available, generated by V. Buch using a highly annealed amorphous ice cluster for the surface and cubic ice for the interior.¹ Comparisons between experimental and simulated spectra have yielded the assignment of the antisymmetric surface-defect modes of the dangling-D ($\sim 2725\text{ cm}^{-1}$), dangling-O ($\sim 2645\text{ cm}^{-1}$), and the surface 4-coordinate D_2O molecules ($\sim 2580\text{ cm}^{-1}$).

1. V. Buch and T. Feldman, Private Communications.

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MF08 15 min 3:54

PREFERENTIAL DEUTERIUM BONDING AT MICROPORE SURFACES OF AMORPHOUS ICE, LANCE DELZEIT AND J. P. DEVLIN

The dangling-OH groups at the surface of microporous amorphous ice bear a significant resemblance to the unbonded OH groups of the acceptor water molecule in the water dimer. Thus, the dimer can be used to gain insight into the behavior of the surface HOD molecules of amorphous ice. Several results have been reported that show the preference for D-bonding over H-bonding within water dimers.^{1 & 2} It has been found that the H-bonded dimers of HOD are approximately 60 cm^{-1} less stable than the D-bonded dimers. Only about 1% D-bonded HOD is present at 20K, but this increased to 3, 9, & 15% at 25, 33, & 50K, respectively.¹

The deposition of HOD at 20K forms an amorphous deposit with nearly statistical distribution of the HOD surface orientation. During warming, this distribution is preserved until 50K where a shift to preferential D-bonding is observed. This shift coincides with the activation of the 3-coord dangling groups. Once past this preferential reorientation, this new distribution is preserved until the dangling groups are eliminated.

1. A. Engdahl and B. Nelander, J. Chem. Phys. 86, 1819 (1987).

2. Brad Rowland, Mark Fisher, and J. Paul Devlin, J. Chem. Phys. 95, 1378 (1991).

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MF09 15 min 4:11
**INFRARED SPECTRUM OF CF₃H ADSORBED ON ALKALI HALIDE FILMS,
C. A. BAUMANN**

The infrared spectrum of trifluoromethane adsorbed onto alkali halide films was observed. The C-H stretch (ν_1) is shifted 42 cm⁻¹ to the blue of the gas phase value, while the C-F stretch (ν_2) is only slightly shifted to the red. There are also noticeable splittings in the degenerate modes (ν_4 , ν_5) that disappear in multilayer coverage.

The effects of substrate and temperature on the observed spectrum will be discussed. The observed vibrational shifts and desorption kinetics will be compared with those derived from the calculated potential of adsorption.

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MF10 10 min 4:28
**LASER EXCITED FLUORESCENCE FROM ORGANIC DYES RELEASED FROM
LIPOSOMES,* P. MISRA, D.L. VANDERMEULEN, AND K.G. SPEARS**

Liposomes are vesicles constituted of phospholipid bilayers dispersed in aqueous media. Owing to their structural similarities to membranes of biological cells, lipid vesicles serve as a model system to study the effects of laser radiation at the molecular level. We have been developing methods for preparing liposomes with dyes either encapsulated in the internal volume (e.g. sulforhodamine) or intercalated in the bilayer membrane (e.g. methylene blue). An important aim of these investigations has been to release efficiently the internal contents of the liposomes by pulsed laser excitation. Excitation by pulsed laser radiation at 532 nm was primarily within the nonfluorescent dimer band of sulforhodamine and resulted in localized heating. A single 8 ns wide pulse at 532 nm caused significant release of liposome contents, being dependent on liposome size, internal dye concentration, and pulse energy density. Methylene blue, which is a membrane-associating dye, was released even more efficiently than sulforhodamine. Time-correlated single photon counting measurements were made to gain insight into the distribution of dye molecules in the interior of the liposome and the bilayer. Potential applications of the technique of laser-mediated release of dyes from liposomes range from targeted release of drugs to localized photothermal release of photosensitizers accompanied by destruction of tumor tissue.

* Financial support from the National Aeronautics & Space Administration (# NASA NAGW-2950) and Howard University's Graduate School of Arts & Sciences is gratefully acknowledged.

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MF11 10 min 4:40

**CONCENTRATIONAL DEPENDENCE OF REVERSIBLE DYNAMIC BLEACHING PROCESSES FOR POROUS SILICATE GLASSES ACTIVATED BY ORGANIC DYE MOLECULES IN STRONG OPTICAL FIELDS,
V. N. BEGER**

It has been revealed that the efficiency of reversible dynamic decreasing of light absorption for organic dye molecules absorbed in porous silicate glass in strong optical field essentially depends on dye molecules concentration. Discovered phenomenon may be explained taking into account processes of nonradiative transfer of electronic excitation energy between adsorbed molecules in conditions of fractal spatial distribution of adsorbed molecules in porous glass. At the same, it has been performed computations that make use of the experimental results on the bleaching processes to evaluate lifetimes of electronic excited states for dye molecules in porous glass as well as in solution.

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MF12 10 min 4:52

STUDY OF ATOMS, IONS AND CLUSTERS OF SUPPORTED SILVER BY THE METHOD OF DIFFUSE REFLECTANCE ELECTRON SPECTROSCOPY, A.N.PESTRYAKOV, A.N.DEVOCHKIN, A.A.DAVYDOV

Variations in atomic, ion and cluster states of silver catalysts for methanol oxidation under the effect of the reaction medium have been studied, using diffuse reflectance electron spectroscopy. Metal atoms and particles were formed on the surface of oxide supports. Spectra of silver catalysts exhibit bands at 240-250, 270, 315-320, 370-390 and 400-460 nm. IR and UV measurements permitted to identify the following silver states: bands at 240-250 nm belong to isolated Ag^+ ions, the 315 nm band can be ascribed to a metallic silver (film and large particles) and the 370-390 nm and 460 nm bands belong to charged silver clusters Ag_n^+ and crystallites of various sizes. EPR studies have not revealed higher valence states in the catalysts. Prolonged treatment of the catalysts by the reaction methanol-air mixture greatly decreases the relative intensity of the band at 315-320 nm, whereas that of the bands at 240-250 and 380 nm rise and there appears a band at 270 nm, characteristic of the charged complexes Ag_2^+ , Ag_3^+ . Increase in the relative intensity of bands at 370-390 and 400-420 nm ascribed to clusters and silver crystallites is accounted for by the development of catalyst surface during the reaction accompanied by the formation of a great number of the above particles already registered using the electron microscopic method. Thus under the effect of reaction medium an active surface of silver catalysts is formed, which manifests itself in the formation of charged forms of Ag^+ and Ag_n^+ , whereas the portion of uncharged metallic silver decreases. Results of the experiments permit to make some conclusions about the nature of active centres of silver catalysts.

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MF13**10 min****5:04**

EXCITON - INDUCED PROCESSES IN SOLID MOLECULAR OXYGEN - NEON SOLUTIONS,
A.G.BELOV, I.Ya.FUGOL', AND E.M.YURTAEVA

The paper is concerned with the processes induced by the trapping of excitons of the neon matrix by impurity centers O and Xe. Binary and triple solutions are studied by a cathodoluminescence spectroscopy method. It is found that the exciton trapping by impurity particles results in an effective dissociation of O₂ molecules, causes an accelerated migration of atoms through the crystal and a desorption of O₂, initiates a defect formation in the vicinity of impurity centers and produces a formation of excimer compounds XeO in triple solutions Ne-O₂-Xe. The mechanisms of these processes associated with the transport of energy of the matrix electronic excitations to an impurity subsystem and its further relaxation are considered. It is shown that all the effects are based on the general principles conditioned by the energy structure and thermophysical characteristics of the Ne matrix- (i) the fast dissipation of exciton excess energy followed by lattice local heating and deformation; (ii) the repulsive behavior of the interaction between Rydberg's excited impurity center and surrounding atoms of the matrix.

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MF14**10 min****5:16**

FLUORESCENCE STUDY OF DEFECT FORMATION via EXCITON TRAPPING INTO MOLECULAR STATES IN RARE GAS SOLIDS, E.V.SAVCHENKO, S.A.GUBIN, O.N.GRIGORASHCHENKO AND A.N.OGURTSOV

Information on defects is very important for elucidation of mass diffusion and chemical reactions in solids. Recently we reported on the pioneering observation of defect formation induced by exciton self-trapping into molecular states in Rare Gas Solids. The paper reports physics of this phenomenon is based on the trapping of electronic excitation energy by the lattice and its conversion to the kinetic energy of atomic motion.

The paper reports new data on molecular hosts in Kr matrix. The electronic subsystem was excited by an electron beam of subthreshold energy at low temperatures. So, the conditions of the experiments excluded the classical knock-on and thermally-activated mechanisms of defect formation. The defects were detected by means of vacuum ultraviolet fluorescence spectroscopy. The experimental study of time evolution of fluorescence spectra revealed a build-up of stable point defects in the samples. It is shown that the defect formation is induced by exciton trapping into molecular states of both the matrix and the impurity centers. The efficiency of defect formation as a factor of the parameters of electronic states of molecular centers was analyzed. The "excited state" mechanism which involves the off-center displacement of molecular center was verified. Based on the experimental data the electronically induced mechanism of mass diffusion was suggested.

1. I.Ya.Fugol', A.N.Ogurtsov, O.N.Grigorashchenko, and E.V.Savchenko
Sov. J.Low Temp.Phys. 18(1), 27 (1992).

2. I.Ya.Fugol', E.V.Savchenko, A.N.Ogurtsov and O.N.Grigorashchenko, Physica B.190,347 (1993)

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MG01 15 min 1:30
THE MICROWAVE SPECTRUM OF DICHLOROSILYLENE SiCl_2 IN EXCITED VIBRATIONAL STATES, MASAHARU FUJITAKE AND EIZI HIROTA

The microwave spectrum of dichlorosilylene in excited vibrational states has been measured in the millimeter- and submillimeter-wave regions. Rotational and centrifugal distortion constants were determined for the ν_1 , ν_2 , $2\nu_2$, and ν_3 excited states of the $\text{Si}^{35}\text{Cl}_2$ isotopic species and for the ν_2 and $2\nu_2$ states of $\text{Si}^{35}\text{Cl}^{37}\text{Cl}$. Analysis of the Coriolis resonance between the ν_1 and ν_3 states of $\text{Si}^{35}\text{Cl}_2$ yielded values of the D Coriolis interaction constant with F constrained and of two higher-order terms and also an accurate value [$5.402338(95) \text{ cm}^{-1}$] of the energy difference between the two excited vibrational states. The rotational constants of $\text{Si}^{35}\text{Cl}_2$ in the first excited states of the three normal vibrations were combined with those of the ground vibrational state reported in a previous paper¹ to obtain the equilibrium structure, harmonic and cubic/third-order anharmonic potential constants.

1. M. Tanimoto, H. Takeo, C. Matsumura, M. Fujitake, and E. Hirota, J. Chem. Phys. **91**, 2102 (1989).

Address of Fujitake: Department of Physics, Faculty of Science, Kanazawa University, Kanazawa 920, Japan.

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MG02 15 min 1:47
Detection and Structure of Carbon-Chain Singlet Molecules, C_nO ($n=5,7,9$), by PDN-FTMW spectroscopy

Teruhiko Ogata, Yasuhiro Ohshima, and Yasuki Endo

Rotational spectra of C_5O , C_7O , and C_9O have been observed by using a Fabry-Perot type Fourier transform microwave (FTMW) spectrometer cooperated with a pulse-discharge-nozzle (PDN). The molecules, produced by the discharge of C_3O_2 diluted in Ar, exhibit a spectrum characteristic of a linear-molecule in a singlet electronic state. For the C_5O molecule, spectra of the normal and all the single isotope substituted species have been assigned, leading to a substitution structure. The r_s -structure and the structure calculated by an *ab initio* MO theory for the C_5O molecule are compared and discussed. The average C-C bond lengths in the C_7O and C_9O molecules have been calculated by assuming the same partial structure as that in the C_5O molecule.

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MG03 15 min 2:04

Detection of Carbon-Chain Triplet Molecules, C_nO ($n = 2, 4, 6, 8$), by PDN-FTMW Spectroscopy

Yasuhiro Ohshima, Teruhiko Ogata, and Yasuki Endo

Rotational spectra of C_nO ($n = 2, 4, 6$, and 8) have been observed by using a Fabry-Perot type Fourier-transform microwave (FTMW) spectrometer cooperated with a pulsed discharge nozzle (PDN). The molecules have been generated by a pulsed electric discharge of C_3O_2 diluted in Ar, and then adiabatically cooled to ≈ 2 K in a subsequent supersonic expansion. All the observed spectra of those species have been analyzed as linear molecules in the $^3\Sigma^-$ electronic ground state. The determined molecular constants, such as rotational, spin-spin coupling, and centrifugal distortion constants, have provided information on the C=C bond lengths, energy gaps between the excited $^1\Sigma^+$ electronic state and the $^3\Sigma^-$ ground state, and rigidity of the molecules in respect of the bending vibrations.

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MG04 15 min 2:21

VIBRATIONAL AND ROTATIONAL LASER SPECTROSCOPY OF SUPERSONICALLY COOLED ALKOXY AND ALKYLTHIO RADICALS,* P. MISRA, X. ZHU, M.M. KAMAL, A.H. NUR, AND H.L. BRYANT, JR.

The alkoxy (RO; $R = CH_3, C_2H_5, i-C_3H_7$) and alkylthio (RS) free radicals are important chemical intermediates in gas-phase atmospheric and combustion chemistry. Laser-induced fluorescence (LIF), in conjunction with a supersonic jet environment, has been used to study the vibrational and rotational spectroscopy associated with electronic transitions involving these radicals. RO radicals were generated *in situ* in the supersonic expansion by excimer laser (KrF @ 248 nm) photolysis of RONO, while RS molecular fragments were produced from similar photodissociation of R_2S_2 . Both Nd:YAG-pumped and excimer-pumped tunable dye laser systems were used to record rotationally-resolved laser excitation spectra of the jet-cooled RO and RS radicals. Wavelength-resolved emission spectra of CH_3O and CH_3S were obtained by exciting the molecules at the wavelength of a strong rotational transition within a vibronic band. Several rotational and vibrational frequencies and parameters obtained from the assignments and least-squares fits will be discussed in the context of the involved molecular spectroscopy of the RO and RS radicals.

* Financial support from the NASA Center for the Study of Terrestrial and Extraterrestrial Atmospheres (# NASA NAGW-2950), U.S. Environmental Protection Agency's Office of Exploratory Research (# R819720-01-0), and the Collaborative Core Unit of Howard University's Graduate School of Arts & Sciences is gratefully acknowledged.

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MG05 15 min 2:38

**VIBRONIC STRUCTURES AND AUTOCORRELATION FUNCTIONS
OF GROUND STATE CH₃O, CD₃O, AND CH₃CH₂O**

A. GEERS, J. KAPPERT, X. LI, C. STÖCK, F. TEMPS, AND J. WIEBRECHT

Stimulated Emission Pumping spectra of the alkoxy radicals CH₃O, CD₃O, and CH₃CH₂O were recorded in a supersonic free jet expansion. The spectra range from the vibrational zero point level up to well beyond the dissociation thresholds. Full rotational resolution is obtained throughout, enabling a detailed vibronic analysis. The vibronic symmetries of states below 3000 cm⁻¹ are assigned by their rotational structures. The energy level scheme is elucidated in terms of a linear Jahn-Teller effect which is active in three modes. Above 4000 cm⁻¹, irregular vibration-rotation structures are observed and evaluated by their autocorrelation functions. These show a rapid initial decay which is attributed to intramolecular energy redistribution (IVR). The obtained IVR time scales are related to the evolution of prepared zero-order states of the ν_3 (C-O stretch) vibration. Evidence is obtained for the occurrence of multiple tier IVR processes. The lifetimes observed are (0.2 ps $\leq \tau \leq$ 3 ps) for CH₃O and (1 ps $\leq \tau \leq$ 10 ps) for CH₃CH₂O. In an energy region with a comparable density of rovibronic states the time evolution of CH₃O appears to be one order of magnitude faster. This demonstrates the influence of the coupling of vibrational angular momenta.

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MG06 15 min 2:55

Electronic Spectroscopy of CF₃O in a Supersonic Jet

Min-Chieh Yang, Xue-Qing Tan, Christopher C. Carter, James M. Williamson, Terry A. Miller, Todd E. Mlsna, J. D. O. Anderson and Darryl D. Desmarteau

The jet-cooled LIF spectrum of the CF₃O $\tilde{A} \leftarrow \tilde{X}$ electronic transition has been observed. Rotational analysis of the high resolution spectrum of the origin band suggests that CF₃O has nominal C_{3v} symmetry in both its ground and first excited state. Vibrational analysis of the dispersed fluorescence spectrum indicates that the Jahn-Teller effect is considerably stronger in CF₃O compared to CH₃O. The details of analysis will be presented.

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INTERMISSION

MG07 15 min 3:30

MULTIPHOTON IONIZATION DIAGNOSTICS FOR FLUORINATED ETHYL RADICALS: STRUCTURAL CONSIDERATIONS FOR DIFLUOROETHYL RADICALS. Jeffrey L. Brum, Russell D. Johnson III, and Jeffrey W. Hudgens

We have carried out calculational and spectroscopic investigations of several fluorinated ethyl radicals. The first electronic spectrum of the α,α -difluoroethyl radical (CF_2CH_3) was observed between 335 nm and 475 nm by resonance enhanced multiphoton ionization (REMPI) spectroscopy. The spectrum arises from two-photon resonances with a 3p Rydberg state. A third laser photon ionized the radicals. The electronic origin is tentatively assigned at $\nu_{00}=43275\text{ cm}^{-1}$ and the vibrational progression is assigned as the $\nu_9'(-\text{CF}_2\text{ wag})=530\text{ cm}^{-1}$. In support of these spectral assignments we report *ab initio* calculations at the MP2/6-31G*, G1, and G2 theory levels which found the optimum structures, vibrational frequencies, and relative energies of CF_2CH_3 , CF_2CH_3^+ , CHF_2CH_2 , and $\text{CHF}_2\text{CH}_2^+$. These results are also discussed in the context of similar work on the analogous fluoromethyl radical (CF_2H).

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MG08 10 min 3:47

DIODE LASER SPECTROSCOPY OF THE JET-COOLED PROPARGYL RADICAL PRODUCED BY THE PHOTOLYSIS OF UV LASER,

Yoshihiro Sumiyoshi, Takashi Imajo, Takehiko Tanaka, and Keiichi Tanaka

The $^1\text{Q}_0$ -branch lines of the ν_6 fundamental band (CH_2 wagging) of the propargyl radical produced in supersonic jet by the 193 nm ArF laser photolysis was observed by time-resolved diode laser spectroscopy.

Propargyl chloride diluted to 3 % with 5 atm Ar was injected into an absorption cell through a 2 mm circular orifice attached to a solenoid-actuated pulsed nozzle with a repetition rate of 25 Hz. The ArF laser (~150 mJ) was introduced to the cell from the direction opposite to the pulsed jet. Focused diode laser beam traveling through a Perry-type multireflection path crossed the supersonic jet just below the nozzle 18 times. The propargyl radical in the jet was well cooled and $^1\text{Q}_0$ lines with low N quantum numbers ($N=1\sim 4$) were observed with appreciable intensities as doublets due to the spin-rotation interaction. The rotational temperature of propargyl in the jet was obtained to be $16 \pm 4\text{ K}$. The time profile of absorption (decay time of about 30 μsec) corresponds to the flight time of the radical across the infrared laser beam.

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MG09 15 min 3:59

Time-resolved Diode Laser Spectroscopy of the ν_6 Band of the Propargyl Radical

Keiichi Tanaka, Takeshi Harada, Kouichi Sakaguchi, and Takehiko Tanaka

The ν_6 (CH_2 wagging) fundamental band of the propargyl radical ($\text{CH}_2\text{C}=\text{CH}$) was observed by time-resolved infrared diode laser spectroscopy. The propargyl radical was produced by the photolysis of allene (C_3H_4) or propargyl chloride ($\text{ClCH}_2\text{C}=\text{CH}$) with 193 nm ArF excimer laser light. More than 120 absorption lines have been assigned to the ν_6 fundamental band of propargyl including $K_a = 1 \leftarrow 0$, $0 \leftarrow 1$, $2 \leftarrow 1$, $1 \leftarrow 2$, and $3 \leftarrow 4$ subbands. Most of the absorption lines were observed as doublets due to the spin-rotation interaction in the 2B_1 ground electronic state.

The rotational and spin-rotation constants for the ground state, $A = 288045.5(34)$, $B = 9365.2766(73)$, $B-C = 316.30(23)$, $\epsilon_{aa} = -544.2(29)$, $\epsilon_{bb} = -11.043(37)$, and $\epsilon_{cc} = -1.0(\text{fixed})$ MHz, are derived from the diode laser spectrum combined with the $10_{1,1} \leftarrow 00_{0,0}$ rotational spectrum by FTMW spectroscopy (1). The vibrational band origin obtained is $687.174\ 89(63)\text{ cm}^{-1}$, which is consistent with the infrared spectrum observed in the argon matrix (2). The molecular constants for the ν_6 state are largely affected by the α -type Coriolis interaction with the ν_{10} (CH_2 rocking) vibration, for example, the rotational and the centrifugal distortion constants A and Δ_K in the ν_6 state change by $-13440(23)$ and $-24.2(21)$ MHz, respectively, from those of the ground state. The figures in parentheses are standard deviation to be attached to the last digit.

- (1) K.Tanaka, Y.Ohshima, and Y.Endo, to be published.
- (2) M.E.Jacox and D.E.Milligan, *Chem. Phys.*, **4**, 45-61(1974).

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MG10 15 min 4:16

Fourier-Transform Microwave Spectroscopy of the Propargyl Radical

Keiichi Tanaka, Yasuhiro Ohshima, and Yasuki Endo

The $10_{1,1} \leftarrow 00_{0,0}$ rotational spectrum of the propargyl radical ($\text{CH}_2\text{C}=\text{CH}$) was observed by a Fourier-transform microwave spectrometer with pulsed discharge nozzle. The propargyl radical was produced by dc discharge ($\sim 1.3\text{ kV}$, 200 mA) of propargyl chloride ($\text{ClCH}_2\text{C}=\text{CH}$) diluted to 0.25 % with 5 atom Ar (0.25 %) and injected into an absorption cell through the pulsed nozzle with the repetition rate of 5 Hz. The rotational temperature of the propargyl was estimated as low as a few K. The rotational transition, $10_{1,1} \leftarrow 00_{0,0}$, observed was splitted into twelve components due to the electron spin-rotation interaction ($J = 1.5 \leftarrow 0.5$ and $0.5 \leftarrow 0.5$) and the hyperfine interaction because of the three H nuclei ($I = 0.5$).

The rotational, centrifugal distortion, and spin-rotation constants for the ground state, $A = 288045.5(34)$, $B = 9365.2766(73)$, $B-C = 316.30(23)$, $\epsilon_{aa} = -544.2(29)$, $\epsilon_{bb} = -11.043(37)$, and $\epsilon_{cc} = -1.0(\text{fixed})$ MHz, as well as the hyperfine interaction constants, α_F , T_{aa} , and T_{bb} , for both the acetylenic ($I=0.5$) and methylenic ($I=1$) protons were derived from the MW spectrum combined with the infrared diode laser spectra of the ν_6 fundamental band (1). The dipole moment of the propargyl radical is estimated to be less than 0.2 D from the microwave power dependence of the spectrum, which agrees with the recent *ab initio* calculation, 0.14 D (2). The figures in parentheses are standard deviation to be attached to the last digit.

- (1) K.Tanaka, T.Harada, K.Sakaguchi, and T.Tanaka, to be published.
- (2) P.Botschwina, private communication.

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MG11 10 min 4:33
FOURIER TRANSFORM MICROWAVE SPECTRA OF THE ALKALI HYDROXIDES GENERATED BY LASER ABLATION

Y. Kawashima, R. D. Suenram, and E. Hirota.

The $J = 1 \leftarrow 0$ rotational transitions of the ground vibrational state of NaOH, KOH, RbOH, and CsOH were observed to determine the nuclear quadrupole coupling constants of the alkali metal atoms using a Fourier transform microwave spectrometer combined with laser ablation to vaporize the samples. In addition to the ground states, the excited vibrational state; $v_2 = 2, l = 0$, was observed for some of the isotopomers. The values of the eQq constants of ^{23}Na , ^{39}K , ^{41}K , ^{85}Rb , ^{87}Rb , and ^{133}Cs atoms were determined from their hyperfine structures. Values of eQq for NaOH and CsOH are reported for the first time and the values for KOH¹ and RbOH² are much improved from the previously reported values.

1. T. T. Raw, T. Yamamura, and C. W. Gillies, J. Chem. Phys., **87**, 3706 (1987).
2. C. Matsumura and D. R. Lide, Jr., J. Chem. Phys., **50**, 71 (1969).

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MG12 15 min 4:45
THE MOLECULAR BEAM OPTICAL STARK SPECTROSCOPY OF CALCIUM MONOHYDROSULFIDE; CaSH, C.T. SCURLOCK, T. HENDERSON, S. BOSELY, K.Y. JUNG, AND T.C. STEIMLE

The rotationally resolved spectrum of the (000-000) $\tilde{B}^2A'' - \tilde{X}^2A'$ band system of a supersonic molecular beam sample of CaSH has been recorded in the presence of a variable static electric field. The magnitude of the α -principal axes components of the permanent electric dipole moment, $|\mu_a|$, was determined to be 5.36(4) Debye and 3.78 (7) Debye for the \tilde{X}^2A' and \tilde{B}^2A'' states, respectively. An analysis of the field free spectrum produced values for the (000) \tilde{B}^2A'' vibronic state fine structure parameters of (in cm^{-1}); $A=10.43356(16)$, $B=0.14343(15)$, $C=0.14114(15)$, $\epsilon_{aa}=-5.7793(19)$, $\epsilon_{bb}=0.10767$, $\epsilon_{cc}=0.03270(83)$. A comparison with the spectroscopic parameters derived from the analysis of the $\tilde{A}^2A' - \tilde{X}^2A'$ band system¹ and a simple one electron molecular orbital picture will be presented.

1. C. N. Jarman and P.F. Bernath, J. Chem. Phys. **98**, 6697 (1993).

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MG13 10 min 5:02

THE MILLIMETER-WAVE SPECTRUM OF CaSH

A. Taleb-Bendiab, F. Scappini, T. Amano, and J. K. G. Watson

We have recorded the pure rotational spectrum of CaSH in the 280-360 GHz region. The spectrum was assigned following the optical work by Jarman and Bernath.¹ The CaSH radical was produced in a high-temperature cell by the reaction of Ca vapor with H₂S in the presence of a DC discharge. The spectrum was analyzed using the *S*-reduced asymmetric top Hamiltonian including the spin-rotation interaction. The rotational and centrifugal distortion constants were extracted from the fit with better accuracy. The spin-rotation parameters, ϵ_{aa} , ϵ_{bb} , ϵ_{cc} , and $|\epsilon_{ab} + \epsilon_{ba}|/2$, were also derived from the fit.

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1. C. N. Jarman and P. F. Bernath, *J. Chem. Phys.* **98**, 6697 (1993).

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MG14 10 min 5:14

A SUPERSONIC MOLECULAR BEAM STUDY OF CaNH₂, K.Y. JUNG, B.-Z. LI, AND T.C. STEIMLE

The (000-000) $\tilde{A}^2B_2 - \tilde{X}^2A_1$ band system of a well collimated molecular beam sample of can₂ has been recorded at a resolution of < 50 MHz FWHM. As in the previous beam study¹, CaNH₂ was produced in a laser ablations/reaction supersonic expansion source. The status of the rotational analysis will be reported and a comparison with the parameters extracted from the analysis of the low resolution LIF spectrum² will be made.

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1. C.J. Whitham, B. Soep, J.-P. Visticot and A. Keller, *J. Chem. Phys.* **93**, 991 (1990).
 2. C.J. Whitham and Ch. Jungen, *J. Chem. Phys.* **93**, 1001 (1990).

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MH01 10 min 1:30

NEW BAND SYSTEM OF YbF MOLECULE

K. N. Uttam and M. M. Joshi

Thermal emission spectrum of YbF molecule has been photographed for the first time in the spectral region $\lambda\lambda$ 3600 – 4600 Å at a reciprocal linear dispersion of 7.3 Å/mm. The study reveals the presence of 103 single and double headed violet degraded bands which have been attributed into two systems viz. C – X and D – X. The system C – X is entirely new and consists of 92 double headed bands while the, already reported, system D – X comprises of 11 single headed bands. The vibrational analysis has been performed and it was found that both the systems arose from the ground state $^2\Sigma$. The detailed analysis shows that system C – X involves the transition $^2\Pi - ^2\Sigma$ while D – X system depicts the feature of $^2\Sigma - ^2\Sigma$ transition. The following vibrational constants have been determined for the different systems :

System	ν_{00}	ω'_e	$\omega'_e x'_e$	ω''_e	$\omega''_e x''_e$	
C ₁ – X	23035.30	523.0	2.00	505.5	1.90	cm ⁻¹
C ₂ – X	23256.00	507.0	2.00	505.5	1.90	cm ⁻¹
D – X	26014.8	574.6	2.80	505.5	1.90	cm ⁻¹

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MH02 15 min 1:42

ANALYSIS OF THE $A^2\Pi-X^2\Sigma^+$ TRANSITION IN YTTERBIUM MONOFLUORIDE

K.L. DUNFIELD, T.E. CLARKE, C. LINTON, A.G. ADAM and J.R.D. PEERS.

High resolution excitation spectra of the $A_1^2\Pi_{1/2} - X^2\Sigma^+$ and $A_2^2\Pi_{3/2} - X^2\Sigma^+$ transitions of YbF have been obtained and the spectra of several isotopomers have been analysed. Among the results to be discussed will be the (1) Λ doubling in the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ states and its correlation with the $B^2\Sigma^+$ state, (2) the spin rotation splitting in the $X^2\Sigma^+$ state and the anomalous splitting in the $v=1$ level, (3) the perturbation in the $v=1$ level of $A_1^2\Pi_{1/2}$ and the analysis of the perturbing state. The experimental results will be discussed in terms of predictions of ligand field theory calculations.

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MH03 10 min 1:59
LASER SPECTROSCOPY OF YF: LINKAGE OF THE TRIPLET STATE MANIFOLD AT 0.03 cm⁻¹ ACCURACY, L. A. KALÉDIN, J. E. McCORD, AND M.C. HEAVEN

The technique of selectively detected fluorescence excitation spectroscopy has been used to record seven electronic transitions of YF. The principal constants (in cm⁻¹) obtained from recent and previous analyses are:

State	Conf.	T ₀	AΛΣ	B ₀	State	Conf.	T ₀	B ₀
³ Π ₁		33292.27(5)	0.0	0.26167(5) <i>f</i>	¹ Δ	4 <i>d5p</i>	31293(30)	0.2704
³ Π _{0e}		33157.64(2)	-134.6	0.26064(2) <i>e</i>	<i>G</i> ¹ Π		31205.811(3)	0.27549(1) <i>e</i>
<i>d</i> ³ Φ ₄	4 <i>d5p</i>	23225.3(50)	404.8	0.27083(3)	<i>F</i> ¹ Σ ⁺		27980.686(6)	0.27533(1)
<i>d</i> ³ Φ ₃	4 <i>d5p</i>	22820.49(2)	0.0	0.27043(4)	<i>E</i> ¹ Π		25464.40(1)	0.270622(2) <i>e</i>
<i>d</i> ³ Φ ₂	4 <i>d5p</i>	22432.21(2)	-388.3	0.27024(4)	<i>D</i> ¹ Π		25324.88(1)	0.26834(1) <i>e</i>
<i>b</i> ³ Π ₂	4 <i>d5s</i>	11769.0(50)	311	0.2775	<i>h</i> ³ Π ₂	4 <i>d5p</i>	25046.9	0.2718
<i>b</i> ³ Π ₁	4 <i>d5s</i>	11457.75(1)	0.0	0.276956(8) <i>e</i>	<i>h</i> ³ Π _{0<i>f</i>}	4 <i>d5p</i>	24955.6	0.2679 <i>f</i>
<i>b</i> ³ Π _{0e}	4 <i>d5s</i>	11270.25(1)	-187.5	0.27478(1) <i>e</i>	<i>h</i> ³ Π _{0e}	4 <i>d5p</i>	24951.5	0.2696 <i>e</i>
<i>a</i> ³ Δ ₃	4 <i>d5s</i>	8206.5(50)	219.0	0.27894(3)	<i>e</i> ³ Π ₁	5 <i>s5p</i>	22928.62(1)	0.27568(9) <i>e</i>
<i>a</i> ³ Δ ₂	4 <i>d5s</i>	7987.53(1)	0.0	0.27807(1)	<i>C</i> ¹ Σ ⁺	4 <i>d5s</i>	19190.35	0.26578
<i>a</i> ³ Δ ₁	4 <i>d5s</i>	7807.61(1)	-179.9	0.27707(1)	<i>B</i> ¹ Π	4 <i>d5s</i>	15885.809(5)	0.26635(1)
<i>X</i> ¹ Σ ⁺	5 <i>s</i> ²	0.0		0.289665(1)	<i>c</i> ³ Σ ₁ ⁺	4 <i>d5s</i>	14430.60(4)	0.26897(5) <i>e</i>

Ligand field theory calculations have been used in an attempt to provide configurational assignments for the excited states.

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MH04 10 min 2:11
LASER SPECTROSCOPY OF ScF: ANALYSIS OF PERTURBATIONS IN THE *F*¹Φ - *A*¹Δ SYSTEM, L. A. KALÉDIN, J. E. McCORD, AND M.C. HEAVEN

The technique of selectively detected fluorescence excitation spectroscopy has been used to record the 0-0 and 1-1 bands of the *F*¹Φ - *A*¹Δ transition of ScF at a resolution of 0.03 cm⁻¹. Perturbations in the *F*¹Φ state caused by interactions with the *h*³Π₂ state were analyzed. With use of a method based on Franck-Condon factors, the vibrational numbering in the perturbing *h*³Π₂ state was estimated. The principal constants (in cm⁻¹) obtained from recent and previous¹ analyses are:

State	v	T _v	B _v	D _v 10 ⁷	T _e	ω _e	B _e	r _e (Å)
<i>F</i> ¹ Φ	1	23518.029(26)	0.358716(6)	6.70(2)	22959.8	623.9	0.363771(8)	1.863
	0	22903.825(11)	0.362110(3)	5.224(3)				
<i>h</i> ³ Π ₂	3	23511.05(6)	0.36153(2)	5.0	21697.7	631.1	0.36842(8)	1.851
	2	22894.011(9)	0.36349(2)	5.0				
<i>A</i> ¹ Δ	1	5181.616(23) ¹	0.361056(3)	4.68(1)	4587.153 ¹	645.23 ¹	0.364752(42)	1.860
	0	4542.235(5) ¹	0.363564(3)	4.686(3)				

Experimentally determined parameters are in excellent agreement with the *ab initio* calculation².

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2. S.R. Langhoff, C.W. Bauschlicher, Jr., H. Partridge *J. Chem. Phys.* **89**, 396 (1988)

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MH05 15 min 2:23

HIGH RESOLUTION FOURIER TRANSFORM EMISSION SPECTROSCOPY OF YH AND YD.

R.S. RAM, AND P.F. BERNATH

The electronic emission spectrum of YH and YD has been investigated in the 690 nm to 3 μ m spectral region using a Fourier transform spectrometer. The YH and YD bands were excited in an yttrium hollow cathode lamp operated with neon gas and a trace of H_2 or D_2 . The observed bands have been classified into three different electronic transitions: $C^1\Sigma^+ - X^1\Sigma^+$, $d0^+(^3\Sigma^-) - X^1\Sigma^+$ and $e^3\Phi - a^3\Delta$. The $d0^+(^3\Sigma^-) - X^1\Sigma^+$ transition of YD could not be identified due to its very weak intensity. The rotational analysis of several bands of the $C^1\Sigma^+ - X^1\Sigma^+$ transition (up to $v''=3$ for YH and $v''=2$ for YD) provides improved equilibrium vibrational and rotational constants for the ground state of YH and YD. The excited $C^1\Sigma^+$ state is involved in several perturbations.

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MH06 10 min 2:40

FOURIER TRANSFORM EMISSION SPECTROSCOPY OF THE $A^1\Sigma^+ - X^1\Sigma^+$ SYSTEM OF YN.

R.S. RAM, AND P.F. BERNATH

The electronic emission spectrum of YN has been observed in the 2.3-2.6 μ m spectral region using a Fourier transform spectrometer. The bands were excited in a yttrium hollow cathode lamp in the presence of a trace of molecular nitrogen. The observed bands, with origins at 3882.7625(4), 4229.0457(3), 4528.6562(46), 4798.5145(13), 5049.4429(20) and 5281.2129(27) cm^{-1} , have been assigned as the 0-0, 1-1, 2-2, 3-3, 4-4 and 5-5 vibrational bands, respectively, of the $A^1\Sigma^+ - X^1\Sigma^+$ electronic transition. The principal equilibrium constants for the ground state obtained from this analysis are $B_e''=0.42815(24) cm^{-1}$, $r_e''=1.80405(50) \text{ \AA}$ and the corresponding excited state values are $B_e'=0.42311(30) cm^{-1}$ and $r_e'=1.81477(64) \text{ \AA}$. This work represents the first observation of the YN molecule.

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MH07 10 min 2:52

FOURIER TRANSFORM EMISSION SPECTROSCOPY HfH AND HfD.

R.S. RAM, AND P.F. BERNATH

The electronic emission spectra of HfH and HfD were investigated in the 476 nm to 1 μ m spectral region using a Fourier transform spectrometer. The bands were excited in a hafnium hollow cathode lamp in the presence of a mixture of neon and H₂ or D₂. For HfH two $\Delta\Omega=0$ electronic transitions with a common $\Omega''=3/2$ lower state, most probably the $X^2\Delta_{3/2}$ ground state, were identified at 14495 cm⁻¹ and 19147 cm⁻¹. These bands have been assigned as the [14.5]3/2 - $X^2\Delta_{3/2}$ and the [19.1]3/2 - $X^2\Delta_{3/2}$ transitions. The rotational analysis of the 0-0 and 1-1 bands of the [14.5]3/2 - $X^2\Delta_{3/2}$ system and the 0-0 band of the [19.1]3/2 - $X^2\Delta_{3/2}$ system provides the following equilibrium constants for the ground state of HfH:

$$B_e'' = 5.01911(8) \text{ cm}^{-1}, \alpha_e'' = 0.12026(11) \text{ cm}^{-1} \text{ and } r_e'' = 1.830691(15) \text{ \AA}.$$

For HfD only the 0-0 band of the [19.1]3/2 - $X^2\Delta_{3/2}$ transition at 19134 cm⁻¹ was identified. This work represents the first observation of the HfH and the HfD molecules.

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INTERMISSION

MH08 15 min 3:20

HYPERFINE AND ISOTOPE STRUCTURE IN THE "ORANGE" SYSTEM OF FeO, M. BARNES, M.M. FRASER, P.G. HAJIGEORGIOU, AND A.J. MERER

The reaction of laser-ablated iron atoms with oxygen or nitrous oxide, under supersonic jet-cooled conditions, is a good source of FeO molecules, which are prepared almost entirely in their ground $X^5\Delta_4$, $v=0$ state. Laser excitation in the 5500 - 6300 \AA region has given strong laser-induced fluorescence spectra of the "orange" system, with sufficient intensity to allow measurement of various bands of the less abundant isotopic molecules ⁵⁴FeO and ⁵⁷FeO. The vibrational structure of the "orange" system, recorded previously¹, has been confirmed, though with the addition of a new weak perturbed band group at 5660 \AA , which has been rotationally analysed. Deperturbation of the more severely perturbed upper levels has given more accurate isotope shift data, which now suggest that the bands must be assigned to two distinct $5\Delta - 5\Delta$ electronic transitions, with (0,0) bands at 6110 and 5583 \AA . The hyperfine splittings of the low J lines of ⁵⁷FeO (2.2% natural abundance) confirm that the electron configuration of the ground state, $\sigma\delta^3\pi^2$, contains an unpaired electron in a σ orbital derived from the Fe 4s atomic orbital; there is no detectable hyperfine splitting in the excited electronic states.

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1. A.S.-C. Cheung, A.M. Lyrra, A.J. Merer and A.W. Taylor, J. Mol. Spectroscopy, 102, 224 (1983).

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MH09 15 min 3:37

ELECTRONIC BAND SYSTEMS OF VCH IN THE 590 - 800 nm REGION, M. BARNES, P.G. HAJIGEORGIOU, A.J. MERER AND G.F. METHA

A complicated system of about 30 bands in the 590 - 800 nm region has been discovered by laser excitation, following the reaction of laser-ablated vanadium atoms with methane under supersonic jet-cooled conditions. At least two electronic transitions must be present, since the most prominent bands are parallel-polarized at the long wavelength end, but perpendicularly-polarized at the short wavelength end. The bands analysed so far have integer rotational quantum numbers, and clear ^{51}V nuclear hyperfine structure. The presence of hydrogen in the carrier is suggested by experiments with CD_4 , but the simple linear-molecule sub-band structure indicates that the carrier is VCH, rather than VCH_3 . The lower state of the strongest bands is an $\Omega = 1$ state, presumably $X^3\Delta_1$ by analogy with VN^1 . Wavelength-resolved fluorescence experiments reveal a highly structured vibrational level pattern in the ground state, with the most prominent peaks corresponding to levels at 146, 572, 840, 1118 and 1402 cm^{-1} . The 840 cm^{-1} frequency is probably the V-C stretching vibration, shifted down considerably from its value in the isoelectronic VN molecule. Consistent with this, rotational analysis has given $B'' = 0.491\text{ cm}^{-1}$, which corresponds to a V-C bond length of about 1.72 \AA , some 0.15 \AA longer than in VN, while the hyperfine h parameter of the ground state (-0.0083 cm^{-1}) is less than half that of VN. The 572 and 1118 cm^{-1} levels seem to involve overtones of the bending vibration, distorted by orbital angular momentum effects, while the 146 cm^{-1} interval is provisionally assigned as the lowest spin-orbit interval of the ground state. Rotational perturbations are widespread throughout the system, even in the bands near 800 nm, while the Λ -doubling in the ($^3\Pi_0$) upper state of the 639 nm band is highly erratic.

1. W.J. Balfour, A.J. Merer, H. Niki, B. Simard and P.A. Hackett, J. Chem. Phys. **99**, 3288 (1993).

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MH10 15 min 3:54

THE OPTICAL SPECTRUM OF A SUPERSONIC MOLECULAR BEAM SAMPLE OF PtN, K.Y. JUNG, AND T.C. STEIMLE

The laser induced fluorescence (LIF) spectrum of a molecular beam sample formed by skimming the products of a Pt ablation/ (NH_3+Ar) supersonic expansion source has been recorded at moderate resolution in the 530nm to 550nm spectral range. In addition to numerous weak spectral features, the strong $\Omega''=0.5-\Omega'=0.5$ transition ($T_{00}=18587\text{ cm}^{-1}$) band system of PtN^1 was readily identified. This system was recorded at high resolution (FWHM < 50 Mhz) in the presence of a variable static electric field. The magnitude of the permanent electric dipole moment for the ground and excited state were determined to be $2.255(9)$ Debye and $0.28(3)$ Debye, respectively, from an analysis of the LIF/Stark spectrum. The observed hyperfine splitting in the high resolution LIF spectrum of $^{195}\text{Pt}(I=1/2)\text{N}$ isotopic form could be most effectively fit to a model that assumed that the ground and excited states are of $^2\Pi$ and $^4\Pi$ symmetry, respectively. An interpretation of the hyperfine parameters in terms of plausible molecular orbital descriptions will be presented.

1. E.J. Frieman-Hill and R.W. Field; (submitted to J. Chem. Phys.)

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MH11 10 min 4:11

THE VISIBLE SPECTRUM OF PLATINUM MONOSULFIDE; PtS, B.-H. Li AND T.C. STEIMLE

The broad banded survey laser induced fluorescence (LIF) spectrum of a molecular beam formed by skimming the products of a Pt ablation/(H₂S+Ar) supersonic expansion source has been recorded in the 530nm to 720nm spectral region. Strong bands at 540nm, 555nm, 611nm and 628nm, are attributed to PtS. The band systems at 540 nm, 555nm and 628 nm have been recorded at high resolution. There was no observed hyperfine splitting in the high resolution LIF spectrum of ¹⁹⁵Pt(I=1)S isotopic form, suggesting that both the ground and excited state have $\Omega = 0$. The band system at 628 nm was fit to a simple $^1\Sigma-^1\Sigma$ model with the determined parameters being (in cm⁻¹ for ¹⁹⁶PtS): $T_0 = 15924.2912(2)$, $B' = -0.13798(3)$, $D' = -1.9(8) \times 10^{-7}$, $B'' = 0.14710$, $D'' = -2.6(9) \times 10^{-7}$. The isotopic shifts of this band system suggest that $v'' = v' = 0$. A comparison with the spectral properties of PtO will be given.

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MH12 10 min 4:23

LASER SPECTROSCOPY OF THE $A^4\Pi - X^4\Sigma^-$ TRANSITION OF MoN

N.S.-K. SZE AND A.S.-C. CHEUNG

MoN was produced by reacting vaporized MoCl₅ and microwave discharged N₂ gas in an oven. Chemiluminescence of pink-blue color was observed. The $A^4\Pi - X^4\Sigma^-$ transition of MoN between 5990-6350 Å has been studied using laser induced fluorescence (LIF) spectroscopy. We have observed in addition to the stronger $\Delta\Sigma = 0$ transitions, the weaker $\Delta\Sigma = \pm 1$ transitions. The use of wavelength-resolved fluorescence spectrum for the assignment of spectral lines and the determination of vibrational constants of the $X^4\Sigma^-$ state will be discussed. Extra lines have been observed in the wavelength resolved LIF spectrum of the $^4\Pi_{1/2} - ^4\Sigma_{3/2}^-$ subband, which indicates that perturbations exist in this component of the $^4\Pi$ state. Molecular constants of both the $A^4\Pi$ and $X^4\Sigma^-$ states will be reported.

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MH13

15 min

4:35

LASER PHOTOACOUSTIC SPECTROSCOPY OF Br_2 VAPOUR IN THE YELLOW-GREEN REGION: R.C.SHARMA AND S.N.THAKUR

Discrete vibronic bands of $\text{B}^3\Pi(\text{ou}^+)$ \leftarrow $\text{X}^1\Sigma_g^+$ transition in the Br_2 vapour imbedded on an underlying continuum primarily due to $\text{B}^3\Pi(\text{ou}^+) \leftarrow \text{X}^1\Sigma_g^+$ transition have been recorded photoacoustically in the frequency region $17740\text{--}19680\text{ cm}^{-1}$. The relative photoacoustic intensities of the bands have been used in estimating the non-radiative de-excitation rates from the upper vibronic levels. It is found that the non-radiative relaxation rate increases with the increasing vibrational quantum number of the $\text{B}^3\Pi(\text{ou}^+)$ state. The relative intensities of the underlying continuum has been interpreted in terms of dissociation from the $\text{B}^3\Pi(\text{ou}^+)$ repulsive state and also from the dissociation of the $\text{B}^3\Pi(\text{ou}^+)$ state. The analysis leads to relative contributions of different mechanisms of non-radiative relaxation in the region of dissociation limit of the $\text{B}^3\Pi(\text{ou}^+) \leftarrow \text{X}^1\Sigma_g^+$ transition viz., dissociation from the excited vibrational level of $\text{B}^3\Pi(\text{ou}^+)$ state, energy transfer from the $\text{B}^3\Pi(\text{ou}^+)$ to the $\text{B}^3\Pi(\text{ou}^+)$ state, direct excitation to the $\text{B}^3\Pi(\text{ou}^+)$ state and non-radiative relaxation from the vibronic level of $\text{B}^3\Pi(\text{ou}^+)$ state.

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MH14

15 min

4:52

MOLECULAR BEAM LASER SPECTROSCOPY OF THE COBALT MONOFLUORIDE MOLECULE

A.G. ADAM, W.D. HAMILTON, S. MATTAR, and M.C. STEEVES.

The electronic spectroscopy of the cobalt monofluoride molecule has been studied using a pulsed molecular beam apparatus. The molecules were produced by chemical reaction of laser-ablated cobalt atoms in a pulsed helium expansion seeded with SF_6 . The spectral region from 680 nm down to 490 nm was searched with a pulsed dye laser ($\sim 0.05\text{ cm}^{-1}$ bandwidth.) Several transitions were discovered in the 540 nm to 495 nm region. Three of the eight molecular bands measured have been tentatively assigned as belonging to a $^3\Pi \leftarrow ^3\Phi$ electronic transition. The assignment of a $^3\Phi$ ground state has been supported by LCAO-LDF calculations. In addition, the strongest of the three assigned bands has been probed at sub-Doppler resolution using a single mode ring dye laser. Hyperfine structure arising from the cobalt nuclear spin, $I=7/2$, has been observed. Analysis of the data is in progress.

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MH15 15 min 5:09

LIF STUDY OF THE ELECTRONIC STATES AND SPECTRA OF BIF
O. SHESTAKOV AND E. H. FINK

BiF radicals produced by reaction of fluorine atoms with bismuth vapour have been investigated by use of the LIF method. Measurements of excitation and fluorescence spectra and of fluorescence decay times have yielded information on several new electronic states and transitions and on radiative lifetimes and transition probabilities. The observed transitions and the basic spectroscopic data of the states are given below.

State	T_e (cm ⁻¹)	ω_e (cm ⁻¹)	$\omega_e X_e$ (cm ⁻¹)	τ_{rad} (μs)	Observed transitions
X ₁ 0 ⁺	0	512.8 ^a	2.38 ^a		
X ₂ 1	6752.8 ^a	543.05 ^a	2.39 ^a	1000(100)	X ₂ →X ₁
a ₂	12084(1)	536(1)	2.2(2)		
A'0 ⁻	22615(20)	387(10)	2.5(2)	50(5)	A'→X ₂
A0 ⁺	22956.9 ^a	383.8 ^a	3.50 ^a	1.5(1)	A→X ₁ , A→X ₂
A''1	24478(4)	388.9(5)	2.16(2)	20(2)	A''→X ₁ , A''→X ₂ ;a
B0 ⁺	26000.8 ^a	625.2 ^a	6.1 ^a	3.0(3)	B→X ₁ ;X ₂
C1	44221(1)	617.6(8)	3.21(16)	~0.085	C→X ₁ ;X ₂ ;a, C→A;A'';B
D ₁ 0 ⁻	43675(10)	616.7(20)	2.9(10)	~0.24	D ₁ →X ₂ , D ₁ →A''
D ₂ 0 ⁺	43693(10)	620.4(20)	4.1(10)	~0.24	D ₂ →X ₂ , D ₂ →A;A'';B

a Literature data.

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TA01 15 min 8:30

**THE B STATE OF THE SODIUM TRIMER:
PSEUDOROTATION, ROTATION, AND CORIOLIS INTERACTION**

WOLFGANG E. ERNST AND STEFAN RAKOWSKY

Due to a pseudo-Jahn-Teller interaction of a $^2E'$ and a $^2A_1'$ state, the lowest potential surface of the B state of Na_3 allows for an almost free pseudorotational motion of the three Na nuclei. In this talk, a summary of the results from resonant two photon ionization and optical-optical double resonance spectroscopy of the B-X system is given. In the X^2B_2 ground state, the molecule has a geometry of an obtuse isosceles triangle, while the B^2A_1' rotational structure reflects an unusual behavior: vibronic states with no excitation of the pseudorotational motion, i. e. vibronic angular momentum $j=0$, indicate shallow minima of the potential surface for an acute triangular shape with 48° bond angle and $r = 4.02(3)\text{\AA}$ bond length. The "equivalent" equilateral triangle would have $r = 3.76(5)\text{\AA}$. States with $j \geq 1$ are pseudorotating with a time constant $\tau < 4\text{ps}$, are approximated best by an equilateral triangle with $r = 3.74(5)\text{\AA}$ and show a large Coriolis splitting of the rotational levels which is described by a term $\pm 2C\zeta K$, C being the rotational constant about the rotational axis of the molecule perpendicular to the plane of the triangle, K the corresponding rotational quantum number and ζ an effective Coriolis coupling constant. Moreover, an effective spin-rotation coupling parameter $\gamma \approx 0.02\text{ cm}^{-1}$ had to be introduced which mainly accounts for the interaction with the nearby $^2E'$ state.

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TA02 15 min 8:47

**HIGH RESOLUTION PHOTODETACHMENT SPECTROSCOPY OF $CCCH_2^-$
K. YOKOYAMA, G. W. LEACH, J. B. KIM, AND W. C. LINEBERGER**

The structure and dynamics of the gas phase $CCCH_2^-$ ion are investigated by high resolution photodetachment spectroscopy using a coaxial laser-ion beam spectrometer. In particular, this molecule supports the unique short-lived excited states in which the electron is weakly bound through its interaction with the large dipole moment of the neutral core (*dipole bound states*). More than 5000 rovibrational transitions were observed and assigned to provide structural information about both the negative ion ground state and the neutral core as well as vibrationally excited states. Examination of the rotational and vibrational state dependencies of the autodetachment linewidths provides dynamical information regarding the detachment process. These linewidths reflect the coupling of the vibrational and rotational degrees of freedom to the weakly bound electron.

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TA03 15 min 9:04

HIGH RESOLUTION ELECTRONIC SPECTROSCOPY OF THE FS_2 FREE RADICAL

Dennis J. Clouthier and Q. Zhuo

Jet-cooled laser excitation spectra of the $\tilde{A}^2A' - \tilde{X}^2A''$ band system of the FS_2 free radical will be presented. This study represents the first spectroscopic observation of this species, which may be important in the dry etching of integrated circuits using SF_6 low pressure plasmas. High resolution spectra of several bands have been rotationally analyzed yielding precise molecular constants and structural data for the ground and electronically excited states. A few axis-switching transitions with $\Delta K_a = 0$ have been assigned, consistent with a calculated axis-switching angle of 5.3° . The electronic transition has $T_{00} = 14\,922\text{ cm}^{-1}$ and involves excitation of a non-bonding electron localized on the terminal sulfur to a π^* orbital delocalized over the S-S bond.

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TA04 10 min 9:21

JET-COOLED SPECTROSCOPY OF Si_2N , DALE J. BRUGH and MICHAEL D. MORSE

A band system or systems have been observed in the $3p$ triatomic nitride Si_2N in the spectral region $33,000\text{ cm}^{-1} - 36,000\text{ cm}^{-1}$ using resonant two-photon ionization spectroscopy. An upper limit of 8.2 eV is placed on the ionization energy of Si_2N . Rotational analysis of the most intense band shows it to be a $^2\Sigma_u^+ \leftarrow ^2\Pi_g$ transition consistent with a linear centrosymmetric structure. The lower and upper state bond lengths have been determined as $r_0''(\text{Si-N}, X^2\Pi_g) = 1.6395 \pm 0.0014\text{ \AA}$ and $r_0'(\text{Si-N}, ^2\Sigma_u^+) = 1.6343 \pm 0.0015\text{ \AA}$. The ground state assignment and bond length are consistent with those calculated by Boldyrev and Simons (personal communication). The molecular orbital configuration is presented and comparison is made to the isovalent $2p$ analogue, CNC.

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TA05 15 min 9:33

ELECTRONIC SPECTRA OF THE HETEROISOTOPIC CH_2D AND CD_2H RADICALS JEFFREY L. BRUM, RUSSELL D. JOHNSON III, AND JEFFREY W. HUDGENS

The $3p\ ^2B_1 \leftarrow \tilde{X}\ ^2B_1$ bands of CH_2D and CHD_2 radicals were observed between 305 and 335 nm by mass resolved, $2 + 1$ resonance enhanced multiphoton ionization (REMPI) spectroscopy. Spectroscopic constants were found for the $3p\ ^2B_1$ Rydberg state of the CH_2D radical ($\nu_{00} = 59940\text{ cm}^{-1}$, $\nu_1\ a_1\ \text{CH}_2\text{ stretch} = 2995\text{ cm}^{-1}$, $\nu_2\ a_1\ \text{CD stretch} = 2220\text{ cm}^{-1}$, $\nu_4\ b_1\ \text{OPLA} = 1260\text{ cm}^{-1}$, $\nu_5\ b_2\ \text{CH}_2\text{ asym stretch} = 3055\text{ cm}^{-1}$, $\nu_6\ b_2\ \text{CD bend} = 1115\text{ cm}^{-1}$) and of the CHD_2 radical ($\nu_{00} = 59920\text{ cm}^{-1}$, $\nu_1\ a_1\ \text{CH stretch} = 3040\text{ cm}^{-1}$, $\nu_2\ a_1\ \text{CD}_2\text{ stretch} = 2150\text{ cm}^{-1}$, $\nu_4\ b_1\ \text{OPLA} = 1165\text{ cm}^{-1}$, $\nu_6\ b_2\ \text{CH bend} = 1210\text{ cm}^{-1}$). Vibrational frequencies calculated by *ab initio* theory agree well with the experimental data.

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TA06 15 min 9:50

SPECTROSCOPY OF HALOGEN AMINE SYSTEMS: DISCHARGE FLOW METHODS AND LOW TEMPERATURE MATRIX ISOLATION, Yevgeniya I. Gershanovich and Julanna V. Gilbert.

The excited electronic states of the halogen amines and of the halogen aminyl radicals are being probed by a combination of discharge flow methods, excimer laser photolysis, and low temperature matrix isolation. In studies carried out by Zhao and Setser,¹ when PF₃ was added to a stream of argon metastables, emission assigned to the PF₂ radical was observed. This method was explored as a way to generate NX₂ radicals from the parent halogen amine. When NFCl₂ is added to a stream of argon metastables, however, NCl(b¹Δ-->X³Σ⁺), NF(b¹Δ-->X³Σ⁺), and Cl₂(D'-->A') emission is observed. These results are compared to excimer laser photolysis studies carried out previously in our laboratory.² Information about the electronic states of NFCl radicals obtained from LIF studies of NFCl in low temperature matrices will also be presented.

1. Y. Zhao and D.W. Setser, Chem. Phys. Lett., 210, 362 (1993).
2. D.B. Exton, S.A. Williams and J.V. Gilbert, J. Phys. Chem., 97, 4326 (1993).

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TA07 10 min 10:07

TRANSIENT FREQUENCY MODULATION SPECTROSCOPY GREGORY E. HALL, TREVOR J. SEARS, JONATHAN C. BLOCH AND ROBERT W. FIELD

A new technique, time resolved frequency modulation spectroscopy, has been used to measure absorption spectra of photochemically generated radicals. As a first example, CN radicals from the 193 nm photodissociation of cyanogen (NCCN) have been detected using a phase modulated continuous wave Ti:sapphire ring laser, probing single rotational lines in the A²Π - X²Σ band system. The sensitivity is significantly higher than could be obtained using a dual beam noise subtraction technique, and in our implementation, we retain sufficient bandwidth to record Doppler broadened lineshapes of collisionless photofragments and accurately follow the time evolution of the lineshape as the fragment radicals collisionally relax to room temperature. We plan to use this spectrometer to record new spectra of CH₂ in the $\tilde{b}^1B_1 - \tilde{a}^1A_1$ band system and also to modify the diode laser absorption spectrometer at Brookhaven to use a variant of the FM technique.

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TA08 10 min 10:19

NEAR-INFRARED ELECTRONIC TRANSIENT ABSORPTION SPECTRUM OF METHYLENE
BOR-CHEN CHANG, MING WU, GREGORY E. HALL, AND TREVOR J. SEARS

Methylene (CH_2) has been the subject of numerous studies since Herzberg and Johns¹ first analyzed the $\tilde{b} \leftarrow \tilde{a}$ electronic spectrum in 1966. The electronic spectrum of CH_2 is complicated by singlet-triplet interactions between the \tilde{a} , \tilde{b} , and $\tilde{X}^3\text{B}_1$ states, the Renner-Teller effect between the \tilde{a} and \tilde{b} states, which correlate with a degenerate $^1\Delta_g$ state at the linear configuration, and spin-orbit coupling. Recently, Green et al.² reported a theoretical investigation of the $\text{CH}_2 \tilde{b} \leftarrow \tilde{a}$ electronic spectrum. In this study, they predicted the positions of many more vibronic bands than were observed by Herzberg and Johns.¹ Although the visible spectrum of CH_2 has been quite extensively studied, there are very few experiments in near-IR region due to less efficient dye laser operation at longer wavelengths. We have constructed a Ti:sapphire laser based transient absorption spectrometer and have measured the $\text{CH}_2 \tilde{b} \leftarrow \tilde{a}$ electronic spectrum between 11400 and 12500 cm^{-1} at Doppler limited resolution. Our spectrum has indeed shown more lines than the previous report.¹ Furthermore, reassignments of several previously observed¹ bands suggested by Green et al.² have been confirmed. The analysis is still in progress. The new experimental data and current state of the analysis will be presented.

Acknowledgment: This work was carried out under Contract No. DE-AC02-76CH00016 with the U. S. Department of Energy and supported by its Office of Basic Energy Sciences, Division of Chemical Sciences.

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INTERMISSION

TA09 10 min 10:50

LASER OPTOGALVANIC TRANSITIONS OF NEON IN THE NEAR ULTRAVIOLET AND VISIBLE,* P. MISRA, X. ZHU, AND A.H. NUR

A pulsed tunable dye laser has been used to excite over 350 optogalvanic (OG) transitions in the wavelength region 337-598 nm using a commercial Fe-Ne hollow cathode discharge lamp. Around 220 of these OG transitions have been identified to be associated with energy levels belonging to neon. Interference fringes obtained simultaneously employing a low-finesse etalon have permitted calibration of the dye laser frequency to within an estimated accuracy of 0.3 cm^{-1} . Several of the observed OG transitions originate from metastable states of neon. A digital oscilloscope was used to record the waveforms of the OG transitions. Polarities of 29 identifiable neon transitions observed in the near UV and visible are understood in terms of processes that affect the population of atoms in metastable states. The OG signals together with the etalon fringes have made possible accurate calibration of rotationally-resolved laser excitation spectra of free radicals in a supersonic jet environment.

* Financial support from the NASA Center for the Study of Terrestrial and Extraterrestrial Atmospheres (# NASA NAGW-2950), U.S. Environmental Protection Agency's Office of Exploratory Research (# R819720-01-0), and the Collaborative Core Unit of Howard University's Graduate School of Arts & Sciences is gratefully acknowledged.

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TA10 15 min 11:02

NEW ELECTRONIC STATES OF THE CHFCI RADICAL

JEFFREY W. HUDGENS, RUSSELL D. JOHNSON III, AND BILIN P. TSAI

The electronic spectrum of the CHFCI radical was observed between 340-420 nm using one color, mass resolved, 2+1 resonance enhanced multiphoton ionization (REMPI) spectroscopy. The spectrum arises from two-photon resonances with the planar $\tilde{F}(3p)$ ($\lambda_{\text{laser}} = 406.7$ nm, $\nu_{00} = 49160(20)$ cm^{-1}) and $\tilde{J}(3d)$ ($\lambda_{\text{laser}} = 361.9$ nm, $\nu_{00} = 55250(20)$ cm^{-1}) Rydberg states. A third laser photon ionized the radicals. Both states produced the same vibrational constants: ν_2 (C-H deformation) = 1280(30) cm^{-1} , ν_4 (C-Cl stretch) = 910(30) cm^{-1} , ν_5 (CFCl scissors) = 440(30) cm^{-1} , ν_6 (OPLA) = 980(30) cm^{-1} . The REMPI spectrum exhibited $\nu'_6 = 1-6$ hot bands of the CHFCI (\tilde{X}^2A) radical. Modeling of these hot bands with a double-well potential yields the inversion barrier, $B_{\text{inv}} = 1180$ cm^{-1} , and the angle between the F-C-Cl plane and the C-H bond, $\Phi_e = 42^\circ$.

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TA11 15 min 11:19

REMPI SPECTROSCOPY OF BF_2

K. K. IRIKURA, R. D. JOHNSON III, AND J. W. HUDGENS

The resonance-enhanced multiphoton ionization (REMPI) spectrum of boron difluoride has been observed. BF_2 is generated by sequential reactions of atomic and molecular fluorine with diborane in a flow reactor. Progressions in ν_2 (bend) are evident, as expected from ab initio calculations. In addition, the adiabatic ionization potential has been calculated to be 8.66 ± 0.05 eV.

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TA12 15 min 11:36

OBSERVATION OF TWO NEW ELECTRONIC STATES OF THE PCl_2 RADICAL

JEFFREY W. HUDGENS AND JEFFREY L. BRUM

Two new Rydberg states of the PCl_2 radical were observed using mass-resolved resonance enhanced multiphoton ionization (REMPI) spectroscopy. The band systems between 440-480 nm and 380-395 nm are assigned to $\tilde{D}^2A_1(4s) \leftarrow \tilde{X}^2B_1$, and $\tilde{E}(4p) \leftarrow \tilde{X}^2B_1$ transitions, respectively. These band systems produce signal through 2+2(\tilde{D}), and 2+1(\tilde{E}) REMPI processes. Analyses yielded the spectroscopic constants: $\tilde{D}^2A_1(4s)$ ($\nu_{00} = 42760 \pm 15$ cm^{-1} , $\nu'_1 = 620 \pm 20$ cm^{-1} , and $\nu'_2 = 230 \pm 20$ cm^{-1}); $\tilde{E}(4s)$ ($\nu_{00} = 51320 \pm 10$ cm^{-1} , $\nu'_1 = 605 \pm 15$ cm^{-1} , and $\nu'_2 = 240 \pm 15$ cm^{-1}) and $\tilde{X}^2B_1(\nu''_1 = 525 \pm 10$ $\text{cm}^{-1})$. Previously reported infrared absorptions [*J. Phys. Chem.* **1969**, *73*, 2774.] are reassigned as $\nu''_1 = 525$ cm^{-1} and $\nu''_3 = 452$ cm^{-1} . Ab initio calculations yielded the optimized geometries, vibrational frequencies, and ionization potentials of PCl_2 (\tilde{X}^2B_1), $\text{PCl}_2^+(\tilde{X}^1B_1)$, and $\text{PCl}_2^+(\tilde{a}^3B_1)$. Ab initio G2 calculations predict the adiabatic ionization potential $\text{IP}_A(\text{PCl}_2) = 8.51$ eV.

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TA13 15 min 11:53

A NEW ELECTRONIC STATE OF THE BCl RADICAL

K. K. IRIKURA, J. W. HUDGENS AND RUSSELL D. JOHNSON III

Mass resolved resonance enhanced multiphoton ionization (REMPI) spectra of BCl radicals were observed between 353 and 357 nm. Rotational analysis shows that the band system arises from $^1\Sigma^+ \leftarrow X^1\Sigma^+$ transitions involving simultaneous absorption of two photons. Using ground state rotational constants obtained from previous microwave data, a rotational analysis yields the spectroscopic constants: $T_0 = 559712 \text{ cm}^{-1}$, $B_0' = 0.7914(2) \text{ cm}^{-1}$ and $D_0' = 1.57(4) \times 10^{-6} \text{ cm}^{-1}$ for $^{11}\text{B}^{35}\text{Cl}$. We have performed *ab initio* calculations at the QCISD(T)/6-311+G(3df)//QCISD(T)/6-311+G* level which predict that $\text{IP}_a(\text{BCl}) = 9.97 \text{ eV}$. Using this theoretical IP_a and solving the Rydberg formula for the proposed origin, we obtain the reasonable solution of $n = 3$ and $\delta = 0.88$ indicating that the upper state is a 3s Rydberg state. Therefore, we designate this state of BCl as the $\text{B } ^2\Sigma^+ (3s)$ Rydberg state.

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TA14 10 min 12:10

HIGH RESOLUTION SPECTROSCOPY OF THE $a^3\Pi_r-X^1\Sigma^+$ TRANSITION OF BCl

K.I. MAHONEY, R.J. BRETT, AND C.WELDON MATHEWS

The $a^3\Pi_r-X^1\Sigma^+$ transition of BCl has been recorded at 0.02 cm^{-1} resolution using a Bruker IFS 120 HR Fourier Transform spectrometer. The $\Delta v = 0$ bands up to $v' = 4$ and $\Delta v = -1$ bands up to $v' = 1$ were observed, and 693 lines were assigned. The increased dynamic range of intensities for the fourier transform spectrometer over photographic recordings has allowed for the first rotational analysis of all four isotopomers of BCl. The most intense band, the 0-0 near $20\,200 \text{ cm}^{-1}$, has been analyzed for $^{11}\text{B}^{35}\text{Cl}$, $^{11}\text{B}^{37}\text{Cl}$, $^{10}\text{B}^{35}\text{Cl}$, and $^{10}\text{B}^{37}\text{Cl}$. The standard deviation of these fittings was about 0.015 cm^{-1} , and the constants are in agreement with previous reports^{1,2}. The other bands are currently be analyzed.

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TB01 30 min 8:30
STRUCTURAL MEASUREMENTS OF ISOLATED CLUSTERS INVOLVING AROMATIC MOLECULES: OBSERVATION OF DIFFERENT ISOMERS AND VIBRONICALLY INDUCED PHOTOISOMERIZATION, T. TROXLER, J.R. STRATTON, P.G. SMITH and M.R. TOPP¹

Van der Waals complexes of perylene with 1-chlorobutane and 1-chloropentane, prepared under supersonic jet conditions, both exist in three isomeric forms. Following vibronic excitation at 355 cm^{-1} , the spectra evolve in the picosecond time domain due to vibrational coupling and conformational change. The time evolution of the emission spectra has been followed via monochromator-resolved spectroscopy and by picosecond-resolution stimulated emission spectroscopy. Following vibrational relaxation, two of the isomers give similarly shaped and broadened fluorescence bands, suggesting rapid isomerization. A third isomer of each complex undergoes similarly rapid vibrational relaxation but does not relax structurally, even at a vibrational energy of 700 cm^{-1} . Picosecond-resolution rotational coherence experiments have measured the structures of all three isomers for both complexes. This study provides for the first time, insights into the isomerization channels that involve large-amplitude motion.

1. Work supported by the NSF (CHE-91-20767) and by the ACS-PRF (24816-AC6)

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TB02 15 min 9:05
STRUCTURAL DETERMINATION OF VAN DER WAALS COMPLEXES OF PERYLENE WITH CYCLOPROPANE USING ROTATIONAL COHERENCE SPECTROSCOPY. J.R. STRATTON, T. TROXLER and M.R. TOPP

Structures for cyclopropane/perylene van der Waals complexes were determined for the 1:1 and 2:1 levels of aggregation. Rotational Coherence Spectroscopy was performed on species red shifted from the perylene origin by 156 , 282 , 300 and 304 cm^{-1} , showing them to be the 1:1 species and 3 isomers of the 2:1 species respectively. The 1:1 species has the sum of the B and C rotational constants equal to $459\text{ Mhz} \pm 1\%$. The 2,0 isomer is a near prolate rotor with $B+C = 359\text{ Mhz}$. The 1,1 isomer at 300 cm^{-1} shows a strong rotation of the inertial axes with $B+C = 368\text{ Mhz}$ and $A = 288\text{ Mhz}$. The 1,1 isomer at 304 cm^{-1} is distinctly different, having no strong axis rotation and $B+C = 388\text{ Mhz}$. An out of plane distance was assumed on the basis of van der Waals radii. Work is presently being done on species red shifted by 422 and 431 cm^{-1} , which are assumed to be the 3:1 species.

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TB03 15 min 9:22
SPECTROSCOPIC OBSERVATIONS OF IVR THRESHOLDS IN MOLECULES WITH INTERNAL ROTATION, Q. JU, S.-P. LU, T.A. STONE, C.S. PARMENTER AND Z.-Q. ZHAO

Two approaches are being used to learn about the onset of intermolecular vibrational redistribution (IVR) as one climbs the S_1 vibrational ladder of aromatic molecules with methyl internal rotation. The three molecules o-, m- and p-fluorotoluene provide a systematic variation in the interaction of the internal rotation with the ring. The molecule p-difluorobenzene serves as a benchmark system with similar ring vibrational structure but no internal rotation. Cold jet $S_1 \rightarrow S_0$ dispersed fluorescence spectra from a series levels about 400 cm^{-1} apart on the S_1 ladders of each molecule show that extensive level mixing in cold S_1 p-fluorotoluene is displayed at a much lower energy (1200 cm^{-1}) than in p-difluorobenzene ($200\text{--}2400 \text{ cm}^{-1}$). Moving the rotor off-axis to the meta position reduces further the onset. Placing the rotor next to the fluorine atom causes little change from the meta behavior. Room temperature spectra in all fluorotoluenes show abundant state mixing at 400 cm^{-1} . We have explored the effect of oxygen quenching (chemical timing) to look at the short-time (psec) spectrum, again as the initial excitation climbs the S_1 ladder. These observations of IVR by the time evolution of structure in the fluorescence spectrum are now in progress so that results must remain state (of Indiana) secrets until the Conference.

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TB04 15 min 9:39
DEEP ULTRAVIOLET FEMTOSECOND MPI STUDIES OF EXCITED STATE DYNAMICS OF NITRIC OXIDE AND CARBON DISULFIDE, I.C. OWRUTSKY AND A.P. BARONAVSKI

Femtosecond deep uv (near 200 nm) pulses were used to directly measure excited state lifetimes for CS_2 and NO in the gas phase. The lifetime of the S_2 state of CS_2 at 205 nm directly measured using femtosecond ultraviolet 1+1 multiphoton ionization spectroscopy is compared to previous indirect lifetime measurements for this state. The deep UV laser pulses have also been used in a time-resolved (2+1) multiphoton ionization study of the two-photon state of NO at 102 nm via a one-photon resonance with the $A^2\Sigma^+(3s\sigma)$ ($v=2$) state. The two-photon excited state lifetime exhibits a strong pressure dependence from which the collisionless lifetime and the bimolecular depopulation or quenching rate constant were obtained. The large quenching rate constant strongly suggests that the state is a medium n Rydberg level in the series converging to the ground state of NO^+ . The subnanosecond collisionless lifetime implies that this state is subject to predissociation and/or autoionization.

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TB05 15 min 9:56

LIFETIMES OF THE \tilde{B} STATE OF CH₃I AND CD₃I USING FEMTOSECOND RESONANCE ENHANCED MULTIPHOTON IONIZATION, A.P. BARONAVSKI AND J.C. OWRUTSKY

Femtosecond pulses in the deep uv (near 200 nm) have been used to directly measure the \tilde{B} state lifetimes for gas phase CH₃I and CD₃I by time-resolved MPI. Tunable deep uv femtosecond excitation pulses were generated by sum frequency generation in BBO of a frequency doubled CPM laser with amplified portions of continuum. For the vibrationless state of CH₃I (CD₃I) the lifetime is 1.38 ps (1.84 psec). It is longer for the $v_3=1$ level of CH₃I (1.80 ps). These values indicate the multidimensional nature of the dissociation and their isotopic and mode dependence will be compared with those obtained by indirect measurements.

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INTERMISSION

TB06 15 min 10:30

FEMTOSECOND MID-IR SPECTROSCOPY USED TO PROBE THE ULTRAFAST DYNAMICS OF LIGAND MOTION SUBSEQUENT TO PHOTODISSOCIATION OF CARBONMONOXY-MYOGLOBIN, T. A. JACKSON, M. LIM, AND P. A. ANFINRUD

Ligand association to and dissociation from the heme prosthetic group [iron (II)-containing porphyrin] of myoglobin (Mb) is essential to its function as an oxygen carrying/storing protein. Elucidation of the motion of the ligand within the hydrophobic interior of the protein and particularly near the iron (called the heme pocket) is important in order to understand the impact that ligand dynamics has on the function of the protein. We have developed a time-resolved mid-IR absorption spectrometer that provides < 250 fs time-resolution, $\approx 3.3 - 5.5 \mu\text{m}$ spectral coverage, 2 cm^{-1} spectral resolution, and sufficient sensitivity to probe the vibrational absorption spectrum of photodissociated CO which provides a sensitive probe of the ligand's external environment. The absorption spectrum of photodissociated CO within the heme pocket of Mb (1) consists of two narrow ($\approx 8 \text{ cm}^{-1}$) features suggesting the CO is well localized, (2) grows with a time constant of $\approx 1 \text{ ps}$ suggesting the motion of the CO is initially diffusive followed by localization near the iron, and (3) remains for $\approx 200 \text{ ns}$ suggesting CO is localized in a very stable "docking site". This "docking site" allows the ligand to bind metastably with protein and may provide a holding bay for the ligand until the protein adopts a conformation favorable for ligand binding or escape.

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TB07 15 min 10:47

DETERMINATION OF THE ORIENTATION OF CARBON MONOXIDE IN THE HEME POCKET OF MYOGLOBIN IN SOLUTION USING TIME-RESOLVED MID-INFRARED SPECTROSCOPY, M. LIM, T. JACKSON, AND P. ANFINRUD

The orientation of carbon monoxide (CO) in the heme pocket of myoglobin (Mb) in ambient temperature solution has been determined by using time-resolved mid-IR spectroscopy. After photolyzing MbCO with polarized visible pulses, polarized IR pulses were used to monitor the change in the absorbance spectra of CO stretch bands. The ratio of perpendicular and parallel polarized absorbencies is directly related to the angle of the CO dipole with respect to the heme normal. The ratio was found to be near unity, suggesting that the CO is either oriented near the magic angle with respect to heme normal or distributed isotropically. The wavelength-dependent polarization anisotropy resolved this issue; the angle of CO is approximately 62 degrees away from the normal to the heme plane

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TB08 10 min 11:04

THEORETICAL CALCULATION OF PUMP-PROBE STIMULATED EMISSION PROFILES OF ULTRAFAST ELECTRON TRANSFER, S. SUZUKI, M. HAYASHI, X. GU, AND S.H. LIN

The photo-induced electron transfer (ET) has been observed in many chemical and biological systems such as photosynthetic reaction center. The time resolved spectra of these phenomenon were well described by many researchers. Recent improvement of femto-second technique lead to the discovery of ultrafast ET's that take place in pico or femto second time scale^{1,2,3}. The conventional theory assumes that the vibrational relaxation of the photoexcited electronic state takes place much faster than the ET process. Considering the typical time scale of the vibrational relaxation (sub-pico second), above assumption should be examined for the cases of ultrafast ET. In this work, the theoretical model in which the ET and the vibrational relaxation are comparable rate will be presented. Also, the pump-probe stimulated emission profiles based on this model will be shown. The various features of these profiles such as quantum beat and temperature effect will be discussed in detail.

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 2. T. Arlt, S. Schmidt, W. Kaiser, C. Lauterwasser, M. Meyer, H. Scheer, and W. Zinth, *Proc.Natl.Acad.Sci.USA*, **90**, 11757 (1993).
 3. G.R. Fleming, J.L. Martin, and J. Breton, *Nature*, **333**, 190 (1988).

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TB09 15 min 11:16

**SOLVENT/SOLUTE INTERACTIONS PROBED BY PICOSECOND TRANSIENT
RAMAN SPECTROSCOPY, D.L. MORRIS, JR. AND T.L. GUSTAFSON**

Picosecond transient Raman spectroscopy provides valuable information about the microscopic interactions that occur between a solute molecule and its solvent environment. In this study, we have chosen 1,4-diphenyl-1,3-butadiene (DPB) as the probe molecule and the linear alkanes from pentane to dodecane as the solvents. Given the virtual degeneracy of the 2^1A_g and 1^1B_u states of DPB in solution, variation of the solvent properties provides valuable information about solvent/solute dynamics, in general. We have obtained the S_1 Raman spectra of DPB in the linear alkane series at two different probe wavelengths (630 and 670 nm). We observe bands assignable to both the 2^1A_g and 1^1B_u states in solution. The spectra exhibit broad ($>50\text{ cm}^{-1}$) Raman bands attributed to motions involving the olefin portion of the molecule. We note that the relative intensities of bands assigned to olefinic stretching motions change as the solvent viscosity increases, and we also observe mode specific, solvent dependent changes in the S_1 spectra with delay.

Based on the S_1 Raman spectra of 1,4-diphenyl-1,3-cyclopentadiene (DPCP), a "stiff" DPB analogue, we attribute the large bandwidths in the S_1 Raman spectra of DPB to a distribution of *s-trans* conformers in solution. The changes in the relative intensities of particular bands with respect to solvent viscosity are believed to arise from differing population distributions of *s-trans* conformers in solution that are dependent on solvent viscosity. The mode specific, solvent dependent changes that occur with delay are attributed to vibrational relaxation of DPB via resonance energy exchange of the excess vibrational energy with the solvent.

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TB10 15 min 11:33

**Solvent-Solute Interactions Probed by Picosecond Transient Raman
Spectroscopy: Excitation Energy Effects and Solvent Dependence of S_1
trans-4,4'-Diphenylstilbene, J.D. Leonard, Jr. and T.L. Gustafson**

We present picosecond transient Raman spectra of 4,4'-diphenyl-*trans*-stilbene (DPS) in dioxane, methylene chloride, toluene, and benzene. We observe mode specific, solvent dependent dynamics in the excited state spectra. In order to investigate the role of vibrational relaxation in this dynamic behavior, we have obtained the time dependence of the S_1 spectra of DPS while varying the excitation energy. We note that the relative intensities of vibrational bands associated with the biphenyl portion of S_1 DPS demonstrate significant changes among the solvents and with time delay. We suggest that the relative intensity changes reflect conformational relaxation associated with the planarity of the adjacent phenyl rings. Bandwidth and peak position changes are also observed in these spectra that we relate to bulk properties of the solvent such as viscosity and dielectric constant. We note a significant Gaussian component in several of the Raman bands which we attribute to a distribution of conformations of the phenyl rings in the excited state.

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TB11 15 min 11:50

RESONANCE RAMAN STUDIES ON EXCITED STATES OF ZN(II) OCTAETHYLPORPHYRIN.
G.Deinum, D.H.Kreszowski and G.T. Babcock

The important biological process of charge separation in the photosynthetic reaction center is initiated by photoexcitation of a chlorophyll molecule into the excited singlet state (S_1). To better understand this process, more insight into the electronic structure and conformation of singlet excited porphyrins is essential. Picosecond time resolved pump-probe Resonance Raman scattering can provide this insight by means of probing bond strengths in the molecule in the excited state. For the experiments we selected Zn(II) Octaethylporphyrin (ZnOEP) because it has several characteristics beneficial for the experiment. In the S_1 state the resonance Raman spectrum is dominated by totally symmetric modes at 1564, 1450, 1359, 1261, 1135 and 664 cm^{-1} . Since nontotally symmetric modes are only weakly enhanced, we conclude that Jahn-Teller distortion is absent in this state. In the lowest triplet state (T_1) nontotally symmetric modes dominate the spectrum. Jahn-Teller distortion in the triplet state thus appears to be important. The latter conclusion agrees with previous results on triplet states that indicated Jahn-Teller distortion in metalloporphyrins with D_{4h} symmetry. Implications of our results for the efficiency of charge separation in the photosynthetic reaction center will be discussed. (Supported by NIH grant GM25480)

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TB12 15 min 12:07

ULTRAFAST SPONTANEOUS AND STIMULATED EMISSION SPECTROSCOPY OF COUMARIN 153: EVIDENCE FOR THE EXISTENCE OF MULTIPLE EXCITED ELECTRONIC STATES, G. J. BLANCHARD, Y. JIANG AND P. K. MCCARTHY

The spontaneous and stimulated emission responses of coumarin 153 in three polar solvents exhibit a substantial excitation energy dependence. The transient spontaneous emission data indicate the presence of multiple closely spaced excited electronic states within the emission profile. Time-domain stimulated emission spectroscopy reveals that the origins of the two radiative electronic states are separated by $\sim 1000 \text{ cm}^{-1}$, and this energy difference is solvent-dependent. The stimulated emission data also point to substantially different Franck-Condon factors for vibronic transitions to each of the excited states. Semi-empirical calculations indicate the presence of at least two singlet excited states within $\sim 1000 \text{ cm}^{-1}$, in addition to several excited triplet states in close proximity to the singlets. Our data, taken collectively indicate that the early-time transient emission response of coumarin 153 in polar solvents is dominated by intramolecular population relaxation between the singlet states that is mediated by their mutual coupling to an excited triplet state.

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TC01 15 min 8:30

**THE MICROWAVE SPECTRUM AND STRUCTURE OF THE DIMETHYLAMINE DIMER:
EVIDENCE FOR A CYCLIC STRUCTURE**

Michael J. Tubergen and Robert L. Kuczkowski

Rotational spectra have been measured for six isotopomers of the dimethylamine dimer using a Fourier-transform microwave spectrometer. No tunneling splittings were observed for either the *a*- or *c*-type rotational transitions and the spectra could be fit to a rigid rotor Hamiltonian including centrifugal distortion terms. Possible dimer structures are discussed and compared to the experimentally determined moments of inertia, dipole moments, and nuclear quadrupole coupling constants. A cyclic structure with C_s symmetry was found to best reproduce the inertial data. The structure of the dimethylamine dimer is compared to the theoretical and experimental structures for the ammonia dimer.

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TC02 10 min 8:47

**HYDROGEN BONDING TO DIMETHYLAMINE: THE MICROWAVE SPECTRUM AND
STRUCTURE OF THE DIMETHYLAMINE-WATER COMPLEX**

Michael J. Tubergen and Robert L. Kuczkowski

Rotational transitions have been observed for four isotopomers of the dimethylamine-water complex using a Fourier-transform microwave spectrometer. Both *a*- and *c*-type transitions were observed. The rotational constants of the four isotopomers are consistent with a structure in which the water acts as a hydrogen bond donor to the dimethylamine ($R_{N\cdots O} = 2.83 \text{ \AA}$). The dipole moment is 2.78 (1) D, and its projections on the principal inertial axes are: $\mu_a = 2.38$ (1) D, $\mu_b = 0.1$ (2) D, and $\mu_c = 1.42$ (1) D. The ^{14}N and ^{17}O nuclear quadrupole coupling constants were measured and their projections onto the inertial axes are compared to predictions based on structural models. Evidence for a nearly free internal rotation will also be discussed.

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TC03 10 min 8:59
**ROTATIONAL SPECTRUM AND STRUCTURE OF THE BENZENE-HCN DIMER,
H. S. GUTOWSKY, E. ARUNAN, T. EMILSSON, AND S. L. TSCHOPP**

Several rotational transitions of the benzene-HCN dimer have been observed with the Balle/Flygare pulsed beam, Fourier transform microwave spectrometer. They are characteristic of a prolate symmetric top and give preliminary values of 1214.1 MHz for B_0 and of 3.97 Å for the c.m. (C_6H_6) to c.m. (HCN) distance. Analysis of the ^{14}N hfs finds $\chi_{aa}(^{14}N)$ to be -4.22 MHz, which corresponds to an average projection angle between the HCN and a-axes of 15.2°. A similar, more approximate value of 22° was found for DF in C_6H_6 -DF.¹ The search for transitions of the benzene-HCN dimer was aided by MMC predictions of the PES and equilibrium structure,² which are in good agreement with experiment. Plans are underway to find and characterize the Ar_3 -HCN tetramer for comparison with the C_6H_6 -HCN dimer.

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2. J. D. Augspurger and C. E. Dykstra, personal communication.

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TC04 15 min 9:11
**ROTATIONAL SPECTRA AND STRUCTURES OF R_g - C_6H_6 - H_2O SANDWICH TRIMERS
(R_g = Ne, Ar, or Kr), E. ARUNAN, T. EMILSSON, AND H. S. GUTOWSKY**

Rotational spectra of R_g - C_6H_6 - H_2O isotopomers, where R_g = Ne, Ar or Kr, have been observed with a Balle/Flygare Fourier transform microwave spectrometer. In these trimers the benzene is sandwiched between the rare gas and H_2O , and $m = 0$ and $m = 1$ internal rotor states are found. Isotopic substitution and inertial analyses show that the R_g - C_6H_6 distance in the trimer is reduced somewhat (~ 0.01 Å), compared to the corresponding distance in the R_g - C_6H_6 dimer. On the other hand, the c.m. (C_6H_6) to c.m. (H_2O) distance in the trimers is increased only slightly (~ 0.003 Å) from its distance in the dimer. Hyperfine structure and substitution analyses with HDO/ D_2O containing isotopomers reveal that the $m = 0$ and 1 states of H_2O in the trimer are virtually unchanged from those in the C_6H_6 - H_2O dimer, including essentially free rotation.¹ Rotational constants for the $m = 0$ state of the parent trimers are as follows:

Trimer	B (MHz)	D_J (kHz)	D_{JK} (kHz)
Ne- C_6H_6 - H_2O	959.350	2.425	13.39
Ar- "	672.778	0.621	3.96
Kr- "	467.775	0.291	1.92

1. S. Suzuki, P. G. Green, R. E. Bumgarner, S. Dasgupta, W. A. Goddard III, and G. A. Blake, Science **287**, 942 (1992).

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TC05 15 min 9:28
**THE MICROWAVE SPECTRUM AND r_0 STRUCTURE OF THE FURAN··H₂O COMPLEX,
A CASE OF LARGE AMPLITUDE MOTION**
F. L. BETTENS*, R. P. A. BETTENS* AND A. BAUDER

The microwave spectra of furan··H₂O and furan··DHO were measured and assigned. The spectra contained direct evidence of large amplitude motions (LAMs). In the spectrum of furan··H₂O, all transitions were split into quartets which were distinguishable as doublets of doublets. The spectrum of furan··DHO was reduced somewhat in complexity with all transitions split into doublets. Two dipolar types of transitions were observed. The presence of quartets in furan··H₂O and doublets in furan··DHO suggested that there were two LAMs occurring in furan··H₂O and that one of these motions was quenched in the complex with DHO. Double resonance was used in both isotopic species in order to distinguish which transitions belonged to the same vibrational state. Each of the six sets of transitions were fitted to the A-reduced Hamiltonian to obtain the effective rotational and centrifugal distortion constants. If the states in furan··H₂O are denoted as 1 to 4, then the inertial defects for states 1 and 2 are similar and are approximately $-0.34 \text{ u}\text{\AA}^2$. For states 3 and 4, $\Delta \approx -0.49 \text{ u}\text{\AA}^2$. Similarly, if the two states observed in furan··DHO are denoted as states 5 and 6, then $\Delta = -0.319$ and $-0.585 \text{ u}\text{\AA}^2$ respectively. These values for the inertial defects imply a planar or nearly planar complex with significant out-of-plane motions. The amplitude of the motions appears substantially larger in states 3, 4 and 6 compared with states 1, 2 and 5, respectively. Further evidence for LAMs in the complex comes from the *very* large values of Δ_{JK} and Δ_K . Effective structures were fitted from the observed rotational constants. The spectral features of this complex, the fitted rotational and centrifugal distortion constants and the effective structures will be presented.

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TC06 15 min 9:45
**CENTRIFUGAL DISTORTION ANALYSIS OF RARE GAS··AROMATIC MOLECULE
COMPLEXES**
R. P. A. BETTENS, R. M. SPYCHER AND A. BAUDER

Centrifugal distortion constants obtained from microwave spectroscopy can be a valuable source of information regarding the van der Waals force field of complexes provided the amplitudes of the van der Waals modes are not too large. In complexes between a rare gas atom and a planar C_{2v} monomer, the complete van der Waals force field is determinable from the quartic centrifugal distortion constants. In such complexes this amounts to 3 diagonal force constants and an off-diagonal bend-stretch force constant. The contribution made to the centrifugal distortion constants of the complex due to the vibrational modes of the monomer can be partially taken into account given the centrifugal distortion constants of the monomer. Using an assumed anharmonic potential function a pseudo- r_e structure can also be determined for the complex. If the x axis is denoted as the axis perpendicular to the symmetry plane of the complex then the planar moment of inertia about this axis (P_x) should be equal to the planar moment of inertia about this same axis in the monomer (P'_x). It can be shown that the difference (ΔP_x) between these two planar moments of inertia is analogous to the inertia defect of a planar molecule in that the anharmonic contribution to this quantity cancels exactly to first order. Hence a comparison between the calculated value of ΔP_x and the observed value gives an indication as to how well a harmonic model approximates the actual van der Waals vibrational motions. The above approach has been applied to the complexes pyridine··Ar, pyrrole··Ar, furan··Ar and 1,1-difluoroethylene··Ar, the results of which will be presented.

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INTERMISSION

TC07 15 min 10:20

**NOVEL CYCLOPROPANE COMPLEXES: CYCLOPROPANE•AMMONIA AND
CYCLOPROPANE•TRIMETHYLAMINE**

Susan E. Forest, and Robert L. Kuczkowski

The microwave spectra of the cyclopropane-ammonia (CYC•NH₃) and cyclopropane-trimethylamine (CYC•TMA) complexes have been observed using a pulsed nozzle, molecular beam Fourier transform microwave spectrometer. Both systems exhibit symmetric top spectra. The spectrum of CYC•NH₃ ($B_0 = 2668.7161$ (4) MHz) is characteristic of free internal rotation, while the internal rotation splitting is absent in CYC•TMA ($B_0 = 1172.2800$ (1) MHz). Each amine interacts with the top of the cyclopropane ring, resulting in a stacked structure which has not previously been observed for cyclopropane complexes. The distance from the center of the cyclopropane ring to the nitrogen for CYC•NH₃ and CYC•TMA is 3.592 (3) Å and 3.4060 (1) Å respectively.

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TC08 10 min 10:37

**EXCITED ν_3 (HCN) VIBRATIONAL STATE OF THE R_g-HCN DIMERS (R_g = Ar, Kr),
E. ARUNAN, T. EMILSSON, AND H. S. GUTOWSKY**

Several rotational studies of excited vibrational states have been published for the Ar-HCN dimer. They include the C-H stretching fundamental ν_1 (HCN)¹ and the van der Waals bending modes Σ_1 and Π_1 .² In the present case, by using an FTMW spectrometer with a pulsed beam, we have observed a linear progression of rotational transitions for Ar/HCN. It is fitted by B_0 and D_J values of 1602.48 MHz and 162 kHz compared to 1609.832 MHz and 172 kHz for the ground state. Similar results have been found for Kr-HCN. In both instances, observation of the excited state required the use of a nozzle heated to 1000°C. The small decrease in B_0 for the new species is consistent with excitation of the C-N stretch in the dimer.

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1. G.T. Fraser and A. S. Pine, J. Chem. Phys. **91**, 3319 (1989).
 2. S. Drucker, A.L. Cooksy, and W. Klemperer, J. Chem. Phys., **98**, 5158 (1993)
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TC09 15 min 10:49

MICROWAVE STUDIES OF ARGON COMPLEXES WITH FULMINIC ACID AND ISOCYANIC ACID, C. BOYCE, C. W. GILLIES, J. Z. GILLIES, F. J. LOVAS, R. D. SUENRAM, AND H. E. WARNER

Complexes of the structural isomers, HCNO (fulminic acid) and HNCO (isocyanic acid), with argon have been studied employing pulsed-beam Fourier-transform microwave spectrometers. Both complexes exhibit predominately b-type rotational transitions. Less intense a-type lines were also observed for the argon isocyanic acid complex. ^{14}N hyperfine structure was resolved for Ar-HCNO, Ar-DCNO, Ar-HNCO and Ar-DNCO. The spectra were fit to a semirigid asymmetric top Hamiltonian with one quadrupolar coupling nucleus. The spectroscopic constants obtained from the fits are: Ar-HCNO (in MHz), $A = 11807.775(2)$, $B = 2010.593(9)$, $C = 1705.380(8)$, $\Delta J = 0.01581(4)$, $\Delta JK = 0.2366(2)$, $\Delta K = -0.0824(4)$, $\delta J = 0.002451(6)$, $\delta K = 0.177(4)$, $\chi_{aa} = -0.130(6)$ and $(\chi_{bb}\chi_{cc}) = 0.358(8)$; Ar-HNCO (in MHz), $A = 11224.568(1)$, $B = 1937.6356(7)$, $C = 1638.6614(4)$, $\Delta J = 0.01470(1)$, $\Delta JK = 0.3888(2)$, $\Delta K = -0.3140(6)$, $\delta J = 0.002464(4)$, $\chi_{aa} = -0.946(4)$, and $(\chi_{bb}\chi_{cc}) = 3.101(7)$. Ar-HCNO is approximately T-shaped and the moments of inertia give an argon fulminic acid center of mass separation of $R_{cm} = 3.49\text{\AA}$ and an angle of 80.2° between R_{cm} and the molecular axis of fulminic acid. The Ar-DCNO isotopic data indicate the oxygen is tilted toward argon. A similar structure is determined for Ar-HNCO from the moments of inertia of the normal isotopomer. In this complex, $R_{cm} = 3.56\text{\AA}$ and the analogous angle between R_{cm} and the a inertial axis of isocyanic acid is 83.3° . The Ar-DNCO isotopic data show the hydrogen is directed toward the argon atom and also provide support for a planar structure.

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TC10 10 min 11:06

THE MICROWAVE SPECTRUM, STRUCTURE AND TUNNELING MOTION OF THE ARGON-KETENE VAN DER WAALS COMPLEX, R. MOLLOY, C. W. GILLIES, J. Z. GILLIES, F. J. LOVAS AND R. D. SUENRAM

Rotational spectra of Ar-CH₂CO and Ar-CD₂CO were observed with a pulsed-beam Fourier-transform microwave spectrometer. Two states exhibiting strong b-type and weak a-type transitions were assigned and fit separately to an asymmetrical top Watson Hamiltonian for each isotopomer. Relative intensities and nuclear spin weights indicate the spectral splitting of transitions arises from an internal rotation about the C=C=O axis of ketene which exchanges the pair of hydrogen (deuterium) nuclei in the two isotopomers. The spectral constants in MHz obtained from the fit for the ground state of Ar-CH₂CO are $A = 10447.926(1)$, $B = 1918.281(40)$, and $C = 1606.703(36)$. The moments of inertia for the two isotopomers give an argon-ketene center of mass separation of $R_{cm} = 3.60\text{\AA}$ and an Ar-cm-C angle of 83° . Although the hydrogen positions are not well determined, the effective geometry is assumed to be planar.

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TC11 15 min 11:18

ROTATIONAL SPECTRA AND INTERNAL DYNAMICS OF $\text{Ar}_2\text{-H}_2\text{O}$, $\text{Ar}_3\text{-H}_2\text{O}$, AND $\text{Ar-(H}_2\text{O)}_3$, E. ARUNAN, T. EMILSSON, AND H. S. GUTOWSKY

The $\text{Ar/H}_2\text{O}$ system is being studied with a Balle/Flygare, pulsed-beam Fourier transform microwave spectrometer. Three new heteroclusters have been identified: a T-shaped C_{2v} $\text{Ar}_2\text{-H}_2\text{O}$, a symmetric top $\text{Ar}_3\text{-H}_2\text{O}$ and a symmetric top $\text{Ar-(H}_2\text{O)}_3$. The $\text{Ar}_m\text{-H}_2\text{O}$ species are very similar to $\text{Ar}_2\text{-HX}$ and $\text{Ar}_3\text{-HX}$ (X=F, Cl), with the main differences attributable to the C_{2v} shape of H_2O versus the linear HX . Thereby the transitions of $\text{Ar}_2\text{-H}_2\text{O}$ are split ~ 90 MHz by tunnelling interchange of the protons while the transitions of $\text{Ar}_3\text{-H}_2\text{O}$ may exhibit both $m = 0$ and $m = 1$ internal rotor states. The spectrum of $\text{Ar-(H}_2\text{O)}_3$ is dominated by the complexities in it of the free cyclic water trimer found by Saykally^{1,2} and may help clarify the tunnelling within the trimer. In addition we have observed a number of transitions which are likely to be those of the $\text{Ar-(H}_2\text{O)}_2$ trimer(s).

1. N. Pugliano and R. J. Saykally, *Science* **257**, 1937 (1992).
2. K. Liu et al, *J. Am. Chem. Soc.*, in press. We thank the authors for a preprint prior to publication.

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TC12 15 min 11:35

THE MICROWAVE SPECTRUM AND STRUCTURE OF THE $\text{CH}_3\text{CN-H}_2\text{O}$ AND $\text{CH}_3\text{OH-HCN}$ DIMERS, F. J. LOVAS, and J. Sobhanadri.

The present studies were motivated by an interest in the effect of hydrogen bonding on the internal rotation barrier in species containing the CH_3 group. The microwave spectrum of the methyl cyanide-water complex, $\text{CH}_3\text{CN-H}_2\text{O}$, and methanol-hydrogen cyanide have been studied with a pulsed-beam Fourier-transform Fabry-Perot-cavity spectrometer. Both species exhibit α -type spectra. Rotational assignments were confirmed from the analysis of the well resolved ^{14}N nuclear electric quadrupole transitions. The methyl cyanide-water complex has a symmetric top spectrum and shows two closely spaced states which arise from tunneling interchange of the water protons and may be characterized by the proton spins as $I = 0$ and $I = 1$. In addition to the normal isotopic form, $\text{CH}_3\text{CN-DOH}$, $\text{CH}_3\text{CN-D}_2\text{O}$, $\text{CH}_3\text{C}^{15}\text{N-H}_2\text{O}$ and $\text{CH}_3\text{C}^{15}\text{N-DOH}$ were studied. Each of the DOH species exhibits only one state as expected. Structural analysis of all five species yields $\text{R(N-O)} = 3.028(2)$ Å and a hydrogen bond distance of $2.072(2)$ Å.

The methanol-hydrogen cyanide complex has an asymmetric top spectrum with A and E symmetry states due to internal rotation of the CH_3 group. For the determination of the structure, additional isotopic variants were studied: $\text{CD}_3\text{OH-HCN}$, $\text{CH}_3\text{OD-HCN}$, and $\text{CH}_3\text{OH-DCN}$. Two H-bonded conformations are possible, i.e. HCN H-bonded to the oxygen of methanol or the methanol hydroxyl H bonded to the nitrogen atom of HCN; the former was detected and an H-bond distance of $2.11(3)$ Å was determined in the structural analysis. The internal rotation splitting has been analyzed by conventional methods to yield an effective barrier, $V_3 = 137.3$ cm^{-1} for $\text{CH}_3\text{OH-HCN}$ and $V_3 = 175$ cm^{-1} for $\text{CH}_3\text{OD-HCN}$. Each of these values are less than one-half of the value for methanol, 373 cm^{-1} . Discussion of the spectral analyses, structure and comparison with other complexes will be presented.

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TC13 15 min 11:52

THE MICROWAVE SPECTRUM AND STRUCTURE OF THE $\text{CH}_3\text{NO}_2\text{-H}_2\text{O}$ DIMER, F. J. Lovas, N. Zobov, W. J. Stevens, G. T. Fraser, and R. D. Suenram

The microwave spectrum of the nitromethane-water, $\text{CH}_3\text{NO}_2\text{-H}_2\text{O}$, complex has been studied with a pulsed-beam Fourier-transform Fabry-Perot-cavity spectrometer. The dominant spectrum is *b*-type with a weaker *a*-type spectrum. Critical to the rotational assignments were well resolved ^{14}N nuclear electric quadrupole transitions, and the incorporation of the pulsed nozzle in one of the mirrors which provided a beam co-axial with the cavity axis to attain linewidths of about 2 kHz. In order to provide structural data, substitutions of HDO and D_2O , and CD_3NO_2 in the complex were assigned. The molecular structure derived from the moments of inertia has a center of mass separation of 3.506(7) Å. The moments of inertia can not distinguish two possible forms of the complex, one with the monomer dipole moment vectors aligned and the other with them anti-aligned. Measurement of the dipole moment components in the complex, $\mu_a = 1.243(11)$ D and $\mu_b = 1.706(12)$ D, resolves this difficulty and shows that the dipole vector are anti-aligned. The *ab initio* results are in excellent agreement with the experimental structure and also show that the form with aligned dipoles has no energy minimum. The complex is quite strongly bonded with a harmonic pseudodiatom stretching force constant $k_s = 9.30$ N/m and evidence for two hydrogen bonds of approximately 2.1 Å between the water O atom and a CH_3 H atom and a water H atom and an O atom of the NO_2 group. Comparison with the transition state geometry in the water catalyzed conversion of nitromethane to its *aci* form, $\text{CH}_2\text{N}(\text{O})\text{OH}$ reported by Melius¹ will be presented.

¹ C. F. Melius, Phil. Trans. R. Soc. London, A **339**, 365 (1992).

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TD01 15 min 8:30

CH₃¹⁸OH: A REVIEW OF FIR LASER LINE MEASUREMENTS AND ASSIGNMENTS, S. ZHAO, R.M. LEES, R.R.J. GOULDING, G. CARELLI, N. IOLI, A. MORETTI, G. MORUZZI, AND F. STRUMIA

The optically-pumped far-infrared (FIR) laser emission from the CH₃¹⁸OH isotopomer of methanol is reviewed from the perspectives of accurate heterodyne laser frequency measurements and line assignment utilizing high-resolution Fourier transform infrared (IR) and FIR spectra. The number of observed FIR laser lines has now reached 105 for this species, 22 of which have been measured in frequency. We discuss the available techniques for identifying the IR-pump/FIR-laser energy level and transition schemes, and their application in obtaining the current list of known assignments for 57 laser lines. As well, we present a list of predicted wavenumbers of potential FIR laser lines for future research interest.

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TD02 15 min 8:47

NEW FIR LASER EMISSIONS FOR METHANOL ISOTOPOMERS PUMPED WITH THE NEW BOULDER CO₂ LASER, LI-HONG XU, R.M. LEES, E.C.C. VASCONCELLOS, AND K.M. EVENSON

Recently, the number of CO₂ laser lines available for optical pumping of far-infrared (FIR) lasers has been significantly increased by the development of a new cw CO₂ laser at the Time and Frequency Division of the National Institute of Standards and Technology in Boulder. This system operates on very high J lines of the normal bands as well as on sequence and new hot-band lines, and has so far generated numerous new FIR laser transitions for CH₃OH, ¹³CH₃OH and CD₃OH. These include the new 123 μm world-record holder from CH₃OH, pumped by the 9HP(20) hot-band CO₂ line, which is now the most efficient known FIR laser line. In this paper, we discuss experimental details and spectroscopic assignments for a number of the energy level systems associated with these transitions.

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TD03 15 min 9:04

FIR LASER ASSIGNMENTS FOR HYDRAZINE BY FOURIER TRANSFORM SPECTROSCOPY, LI-HONG XU, J.T. HOUGEN, J.W.C. JOHNS, AND Z.F. LU

The Fourier transform infrared spectrum of hydrazine ($\text{H}_2\text{N-NH}_2$) has been recorded between 800 and 1400 cm^{-1} on the modified DA3.002 Bomem spectrometer at a resolution of 0.003 cm^{-1} at the Herzberg Institute of Astrophysics, National Research Council, Ottawa. The strong antisymmetric amino-wagging band overlaps with the CO_2 laser bands including the hot bands. Numerous FIR laser emissions have been reported. This paper presents current progress in assigning some of the FIR laser lines by the FTS method.

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TD04 15 min 9:21

A NEW "RITZ" PROGRAM FOR DIRECT ENERGY LEVEL FITTING AND FIR LASER LINE PREDICTION, G. MORUZZI, AND LI-HONG XU

We have developed a new program for the assignment of the FT methanol spectrum. The energies of the levels connected by the assigned transitions are evaluated by the Rydberg-Ritz combination principle. That is, we evaluate the energy level values E_i which minimize the expression

$$\chi^2 = \sum_{i,j} \frac{(E_i - E_j - \nu_{ij})^2}{\epsilon_{ij}^2}$$

where E_i and E_j are the energies of the i th and j th level of the molecule, respectively, ν_{ij} is the experimental wavenumber of the corresponding transition, and ϵ_{ij} its experimental accuracy. Very accurate values for the energies of the levels (accuracies of the order of 10^{-4} cm^{-1}) are thus obtained. Transitions connecting to a new level can be predicted by parabolic extrapolation, and the procedure is iterated. This program has been used for assigning more than 21 000 absorption lines of CD_3OH and for checking 36 000 assignments of the parent species CH_3OH . The energies of the CO-stretch levels obtained from the assignments of the IR transitions can be used for predicting new FIR laser lines. This, combined with the development of new pumping sources in the IR¹, can highly facilitate the choice of new laser sources in the FIR region.

1. K.M. Evenson, private communication.

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TD05 10 min 9:38

A WAVELENGTH METER FOR INFRARED DIODE LASER, EIZI HIROTA, KAZUO HAYAKAWA, MISAKI OKUNISHI, AND CHIKASHI YAMADA

In order to facilitate spectroscopy using infrared diode lasers as sources, we have constructed a wavelength meter which readily allows us to determine the wavenumber of a laser line to an accuracy of 0.1 cm^{-1} . This accuracy makes correspondence with reference spectra much easier. The meter is essentially a Michelson interferometer similar to that reported previously¹, but its structure has been simplified by employing a linear encoder as a wavelength standard. Counting fringes in this way resulted in wavenumbers with the expected accuracy. We also showed by Fourier transformation of the fringe pattern that we might diagnose the multimode oscillation of a laser diode.

1. K. Nagai, K. Kawaguchi, C. Yamada, K. Hayakawa, Y. Takagi, and E. Hirota, J. Mol. Spectrosc. 84, 197 (1980).

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TD06 15 min 9:50

AUTOMATED WAVENUMBER DETERMINATION FOR DIODE LASER SPECTRA, LI-HONG XU, R.M. LEES, AND G. MORUZZI

An accurate and convenient two-channel wavenumber calibration program has been developed for a Laser Photonics diode laser system. The method is based solely on comparison of sample and reference spectra, as recorded and stored by the standard sweep control and data acquisition facilities supplied with the system. The calibration program reads the sample and reference data files in Laser Photonics format, extracts the spectral data, and converts them into standard IEEE data format. A simple procedure is implemented for peakfinding, with the sample peak wavenumbers calculated from a calibration curve determined by least squares fitting to the reference wavenumbers. Provided the reference spectrum has a suitable distribution of peaks, a calibration precision of $\pm 0.0002 \text{ cm}^{-1}$ or better is obtained over the full width of the diode laser scan, of the same order as the original standard reference. Given the rapid ongoing improvement in availability of good reference spectra for all regions, this program offers a simple, reliable and automatic procedure for accurate measurement of diode laser data.

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INTERMISSION

TD07 15 min 10:20
PULSED MILLIMETER AND SUBMILLIMETER WAVE GENERATION
W. GUO, J. C. SWARTZ, J. M. DUTTA, C. R. JONES, B. D. GUENTHER, AND F. C. DE LUCIA

Prebunched electrons from 1 MeV and 40 MeV electron gun systems have been used to produce short pulses of spectrally pure millimeter and submillimeter waves. Several microwave couplers, including waveguide and Orotron geometries, were used to demodulate the picosecond structure of the electron beam. The spectral extent and purity of the signal generated were measured by use of a Fourier transform spectrometer and spectrum analyzer, respectively. The design and test of the Orotron cavity and its periodic structure will be presented.

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TD08 15 min 10:37
ORIENTATION MODULATION IN FOUR-LEVEL INFRARED-INFRARED DOUBLE RESONANCE IN METHYL FLUORIDE AND AMMONIA, GLENDAM. SORIANO AND R. H. SCHWENDEMAN

Four-level IR-IR double resonance spectra of $^{13}\text{CH}_3\text{F}$ and $^{15}\text{NH}_3$ were taken under conditions of population modulation with circularly polarized pump and probe radiation using the method of Shin and Schwendeman.¹ For population modulation, a mechanically-chopped pump beam was fixed at either right or left circular polarization while the probe beam was kept at fixed circular polarization. Four-level double resonance spectra were also taken under conditions of orientation modulation in which the polarization of the pump beam was switched between right and left circular polarization by an electro-optic crystal modulator while the circular polarization of the probe beam was fixed. Thus, the difference in intensity between spectra taken under population modulation with right and left circularly polarized pump beam was observed directly with orientation modulation. The difference is direct evidence for partial conservation of the spatial orientation of the angular momentum during collision-induced rotational transitions. It can be shown that the intensity of the spectrum recorded under orientation modulation is proportional to the $n=1$ spherical tensor combination of the populations (orientation) of the degenerate m states of the lower level of the probe transition. Orientation modulation spectra are observable only when the quantum number k for the component of the angular momentum referred to the molecule-fixed symmetry axis is the same for the upper level of the pump and lower level of the probe transitions. The data were fit to theoretical lineshapes that were calculated by assuming that the tensor combinations created in the upper level of the pump transition were transferred intact to the lower level of the probe transition by collision. Analysis of the lineshapes shows that a loss of orientation occurs during collision-induced transitions. Also, only transitions that result from collisions that occur with large impact parameters and therefore cause little change in the velocity of the molecules show a tendency for conservation of the orientation. A description of the apparatus and samples of the observed spectra will be included in the discussion.

1. Uhyon Shin and R. H. Schwendeman, J. Chem. Phys **96**, 8699 - 8712 (1992).

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TD09 15 min 10:54

STARK SPECTROSCOPY USING THE WATER VAPOR LASER

M. JACKSON, G. R. SUDHAKARAN, R. M. LEES, AND I. MUKHOPADHYAY

A far-infrared (FIR) water vapor ($\text{H}_2\text{O}/\text{D}_2\text{O}$) laser has been developed to perform laser Stark spectroscopy. The FIR laser has been modified from an existing HCN/DCN laser system and consists of a 4 m long, 10 cm diameter laser cavity with copper reflectors against its ends. The active medium is a $\text{H}_2\text{O}:\text{H}_2$ or $\text{D}_2\text{O}:\text{D}_2$ gas mixture. CW laser oscillations at $\lambda = 118.6 \mu\text{m}$ for H_2O and $\lambda = 107.7 \mu\text{m}$ for D_2O have been observed. A reliable output power of 25 mW with stable plasma and a good signal to noise (S/N) ratio has been achieved for both laser lines.

The laser Stark spectrum for CH_3OH has been observed for the first time up to 50000 V/cm using the H_2O and D_2O laser lines.

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TD10 15 min 11:11

DIODE-LASER MOLECULAR BEAM SPECTRUM OF THE ν_2 NO STRETCHING BAND OF CHLORINE NITRATE, Anne M. Andrews, José L. Domenech, Gerald T. Fraser, Walter J. Lafferty, Richard D. Suenram and Patricia Watson.

Chlorine nitrate serves as a temporary reservoir of both chlorine and odd nitrogen in the stratosphere since it is formed by the reaction of NO_2 and ClO and removes Cl atoms from ozone destructive reactions. Unresolved IR spectra of this molecule have been recorded by several laboratories; however, partially resolved rotational spectra are reported in only one study, that of the ν_4 band at 779 cm^{-1} . Complete spectral resolution of ClONO_2 at room temperature is hindered by numerous "hot bands" originating mostly from levels of the very low frequency torsional band. The goal of this work is to obtain the spectroscopic constants for the ν_2 band at 1293 cm^{-1} at low temperatures in a supersonic jet where the "hot band" lines are suppressed in order to model its strong Q-branch feature at stratospheric temperatures.

A molecular beam system coupled with a diode laser spectrometer was used in this study. The sample used was prepared by the reaction of ClF with dry nitric acid and purified by trap-to-trap distillation. About 10% ClONO_2 was mixed with argon. The molecular beam was produced by passing this mixture through a 1 inch pulsed slit nozzle. The laser beam was passed through the jet 6 times to increase the absorption path length.

Although we have only preliminary results at this writing, the ν_2 band appears to consist entirely of A-type transitions. The P- and R-branch transitions are completely resolved, and their assignment verified by comparing ground-state combination differences with those calculated using ground-state rotational constants determined by microwave spectroscopy². The Q-branch region consists of a series of subband Q-branches in which the J structure is unresolved; however the profile of these Q-branches can be reproduced using the spectroscopic constants obtained from the P- and R-branch regions. Transitions with J up to 22 and $K_a \leq 11$ have been observed. Comparison of calculated and observed spectra indicates that the beam temperature is about 15 K.

1. W. Bell, G. Duxbury and D. D. Stuart, J. Mol. Spectrosc. **152**, 283 (1992).

2. R.D. Suenram and F.J. Lovas, J. Mol. Spectrosc. **105**, 351 (1984).

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TD11 15 min 11:28

ACCURATE FAR-INFRARED FREQUENCIES FOR PURE ROTATIONAL AND FINE-STRUCTURE TRANSITIONS IN THE $^2\Pi$ ELECTRONIC GROUND STATE OF NITRIC OXIDE, NO

F. STROH, T.D. VARBERG, AND K.M. EVENSON

The far-infrared spectrum of the NO radical in its electronic ground state exhibits both pure rotational transitions and magnetic dipole transitions in P -, Q - and R -branches between the two spin states $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$. We have measured 150 transitions using tunable far-infrared spectroscopy to supply accurate far-infrared frequencies for the stronger pure rotational and magnetic dipole transitions as well as to check on intensity predictions for perturbation allowed electric dipole transitions between the spin states.

Two stabilized CO₂ laser frequencies were mixed with a tunable microwave frequency in a metal-insulator-metal (MIM) diode to generate far-infrared radiation. To obtain accurate center frequencies Voigt profiles were adjusted to the observed absorption spectra by a least-squares procedure. This technique was shown to supply center frequencies accurate to better than 10 kHz for the CO molecule^a.

Fits of the obtained transition frequencies to an effective Hamiltonian of the type introduced by Brown et al.^b have been performed. Standard deviations somewhat higher than 10 kHz have been found for these fits up to now. The reason for that is under investigation and will be discussed at the meeting. The preliminary value for the spin-orbit coupling constant is 3691 813.743 (21) MHz, which is a factor of 50 more accurate than the one determined from the most recent Fourier transform measurement^c.

^aT.D. VARBERG AND K.M. EVENSON, *Ap. J.*, **385**, 763-765 (1992).

^bJ.M. BROWN, M. KAISE, C.M.L. KERR, AND D.J. MILTON, *Mol. Phys.*, **36**, 553-582 (1978).

^cA.H. SALECK, G. WINNEWISER, AND K.M.T. YAMADA, *Mol. Phys.*, **76**, 1443-55 (1992).

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TD12 15 min 11:45

ROVIBRATIONAL ENERGY TRANSFER IN HIGHLY VIBRATIONALLY EXCITED CH₄
Jody Klaassen, Steve Coy, Ilya Dubinsky, Jeff Steinfeld, and Bernd Abel

We have developed a new form of PUMP-PROBE double resonance applicable to non-polar non-fluorescing species like CH₄, for use in collisional energy transfer measurements and spectroscopic studies. CH₄ has been the subject of few double-resonance studies because of a lack of pump sources and of low-noise probes.

We use a pulsed, Raman-shifted Ti-S source as the pump, and MBE, LN₂-cooled lead salt diode lasers as a probe. The STI (now Continuum) HRL-100 Ti-S laser produces Fourier-transform-limited 2-3 nsec pulses from 720-950 nm with midband energies of 40-50 mJ. Using a 2.5 m H₂ Raman cell with a single refocusing lens, under weakly-focussing conditions we achieve outputs of 2-3 mJ at 4300 cm⁻¹ (CH₄ $\nu_3 + \nu_4$ band) with minimum rotational Raman. The MBE diode is lower in noise by a factor of 10 than He-cooled types and covers the 2970 cm⁻¹ region, allowing probes on the $\nu_3 \leftarrow 0$ and $\nu_3 + \nu_4 \leftarrow \nu_4$ bands.

Most of the data obtained has been on single-state-resolved rovibrational relaxation in the $\nu_3 + \nu_4$ manifold, and in the ground state. Since both ν_3 and ν_4 are F₂ vibrations with $\ell = 1, 0, -1$, resulting in no nuclear-spin-forbidden levels, energy transfer is complex. At high pressures, when populating the 2-- A₁ $\nu_3 + \nu_4$ level via $\nu_3 + \nu_4 \leftarrow 0$ and probing the same level using $\nu_3 + \nu_4 \leftarrow \nu_4$, the several rates visible in the decay rule out the simplest models and indicates that the effective rotational partition function is larger in $\nu_3 + \nu_4$ than in ν_4 (Fig. 1). We will present the vibrational energy transfer analysis and discuss the current state of rotational energy analysis.

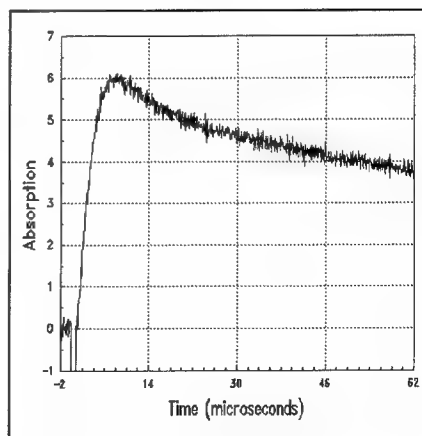


Figure 1. CH₄ relaxation of 2-- A₁ level of $\nu_3 + \nu_4$ at 0.8 Torr.

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TE01 15 min 1:30

ROVIBRATIONAL SPECTRA OF THE STRETCHING FUNDAMENTAL OF CCl₄

Songlin Xu, R. S. McDowell, and S. W. Sharpe

The stretching fundamental, ν_3 , of CCl₄ at 13 μm is difficult to resolve because of hot-band structure, overlapping due to the natural chlorine isotopic mix, and a Fermi resonance with $\nu_1 + \nu_4$. We have recorded spectra of 1% CCl₄ in argon, expanded through a 12-cm-long slit, with a tunable diode laser and an effective path of ~ 3 m through the expansion. At the resulting effective temperature of ~ 10 K, we observe fully-resolved rovibrational structure of the spherical top C³⁵Cl₄, the symmetric top C³⁵Cl₃³⁷Cl, and the asymmetric top C³⁵Cl₂³⁷Cl₂, using natural isotopic CCl₄. These bands have been analyzed, and the spectroscopic and molecular constants will be reported and discussed.

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TE02 15 min 1:47

SUB-DOPPLER OPTOTHERMAL SPECTROSCOPY AND INTRAMOLECULAR DYNAMICS OF THE ν_1 AND $2\nu_1$ BANDS IN SF₅CCH

M. Becucci, J. E. Gambogi, J. H. Timmermans, K. K. Lehmann, G. Scoles and G. L. Gard

The high resolution spectra of the fundamental and first overtone of the acetylenic CH stretch in SF₅CCH have been measured in a collimated molecular beam. The fundamental spectrum ($\rho_{A1} = 191/\text{cm}^{-1}$) is only slightly perturbed at low J, K corresponding to an "effective" lifetime of 2 nsec. Four other weak bands are present in this region and their origin is hypothesized as being due to isotopes and near resonant perturbing states. In the spectrum of the first overtone ($\rho_{A1} = 1 \times 10^5/\text{cm}^{-1}$), the features have a Lorentzian lineshape and from their average width an intramolecular vibrational relaxation (IVR) lifetime of 1.5 nsec is calculated. The long lifetimes of both bands can be explained by the lack of low order anharmonic resonances.

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TE03 15 min 2:04

INTRACAVITY LASER ABSORPTION SPECTROSCOPY IN THE NEAR INFRARED WITH DOPPLER LIMITED RESOLUTION.

A.KACHANOV, B.ABEL, J.TROE, F.STOECKEL.

Intracavity laser spectroscopy (ICLAS), since its introduction in early 70th, has been considered by most of the spectroscopists as an extremely sensitive, but rather complicated technique with many nonlinearities involved.

We intend to show that it is neither complicated, nor nonlinear. The performance of a solid-state intracavity laser spectrometer for the study of highly excited vibrational states of both stable and unstable species as well as for time-resolved studies of chemical reactions on the sensitivity limit up to 10^{-13} cm⁻¹ will be demonstrated. For analytical applications the IR ICLAS promises to be more versatile, less complicated, less expensive and up to three orders of magnitude more sensitive than frequency modulated diode laser spectrometers.

A comparative analysis of the ICLAS and other highly sensitive methods of measuring absorption spectra will be made.

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TE04 15 min 2:21

DEVELOPMENT, JUSTIFICATION AND APPLICATIONS OF A MID-INFRARED POLARIZATION DIVISION INTERFEROMETER, PRASAD L. POLAVARAPU, GANG-CHI CHEN AND STEPHEN WEIBEL

We report the development of a polarization division interferometer (PDI) for the mid-infrared region. This interferometer uses a self-designed beamsplitter constructed in-house from a BaF₂ polarizer and a matching substrate. In conjunction with a linear polarizer in front of the source and two roof-top mirrors one in each arm of the interferometer, PDI divides the input beam into two orthogonal linear polarization components, recombines them for interference at the beamsplitter and directs the output beam at 90° to the direction of input beam. Light exiting the interferometer is manipulated entirely with lenses, to avoid polarization distortions that are inherent to the reflecting surfaces of the mirrors. Details of the instrumental design for this mid-infrared PDI are presented. The performance of PDI is evaluated by measuring the circular dichroism of α -pinene and camphor, and linear dichroism of oriented polypropylene and polystyrene. These measurements establish the utility of PDI to measure transmission, circular dichroism and linear dichroism spectra without need for any additional components. The dichroic multiplex advantage (ability to measure dichroism in the entire mid-infrared region from a single measurement) and throughput advantage are demonstrated.

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TE05 15 min 2:38**POLARIZATION DIVISION INTERFEROMETRY: FAR INFRARED DICHROISM, PRASAD L. POLAVARAPU, AND GANG-CHI CHEN**

Polarization modulation in the far infrared region is not easily achieved due to the strong far infrared absorbance of the material based optical elements. Polarization division interferometry (PDI) overcomes this problem in a unique way. Using a far-infrared PDI developed in our laboratory, the performance of PDI is evaluated by measuring the circular dichroism of α -pinene, camphor and 3-methylcyclohexanone and linear dichroism of oriented polyvinylfluoride. These measurements establish the utility of PDI to measure transmission, circular dichroism and linear dichroism spectra in the far-infrared region (~ 600 - 10 cm^{-1}) without need for any additional components. The dichroic multiplex advantage (ability to measure dichroism in the entire far-infrared region from a single measurement) and throughput advantage are demonstrated.

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TE06 15 min 2:55**POLARIZATION DIVISION INTERFEROMETRY: TIME RESOLVED INFRARED DICHROISM, PRASAD L. POLAVARAPU, AND GANG-CHI CHEN**

Polarization division interferometry (PDI) offers unique advantages over conventional interferometric techniques. Since PDI measures dichroism directly at the interferometer frequencies, it becomes possible to investigate time resolved infrared dichroism for the first time. Using a mid-infrared PDI developed in our laboratory, the time resolved infrared dichroism has been measured in μs time scale for the first time. The time resolved measurements on the function of a photoelastic modulator and on the behaviour of nematic liquid crystal in the presence of external electric field are presented as the first examples. These measurements establish the feasibility of time resolved infrared dichroism measurements and open boundless opportunities for studying the temporal behaviour of biomembranes in the presence of external stimulus.

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TE'01 15 min 3:30

FINE AND HYPERFINE STRUCTURE OF THE X $^2\Pi_{\Omega}$ ELECTRONIC STATE OF HBr^+ , A. CHANDA, W.C. HO, F.W. DALBY and I. OZIER

The vibration-rotation spectrum of the X $^2\Pi_{\Omega}$ electronic state of H^{79}Br^+ and H^{81}Br^+ has been studied in the frequency range from 1975 cm^{-1} to 2360 cm^{-1} with an a.c. glow discharge using velocity modulation. Transitions involving v ranging from 0 to 5 and J up to 18.5 were observed in both the $\Omega=1/2$ and $\Omega=3/2$ spin substates. For the two isotopomers, a total of over 600 vibration-rotation lines were measured. Since the vibrational spacings are of the same order of magnitude as the spin-orbit splitting in this inverted $^2\Pi$ system, significant non-resonant mixing occurs between rotational levels of ($^2\Pi_{1/2}, v$) and ($^2\Pi_{3/2}, v+1$) states. This gives rise to anomalous Λ -doubling in the rotational energy levels of all vibrational states except the ($v=0$) state of the $^2\Pi_{3/2}$ spin substate, which is isolated and unique. A striking example of this effect on the observed spectrum is the unusual J -dependence of the splitting of the two Λ -doublets belonging to the fundamental band of the $^2\Pi_{3/2}$ substate. The structure of the usual Hamiltonian¹ for a $^2\Pi_{\Omega}$ state has been modified and the third order vibrational Van Vleck transformation included to account for this interaction, so that reliable molecular parameters could be determined. In addition, a complete analysis of the hyperfine splittings arising from magnetic dipole and electric quadrupole interactions has been carried out for low J transitions of both the Ω substates. The hyperfine coupling constants have been determined and an improved description of the distribution of the unpaired electron in the molecule has been obtained. Details of the experiment, the modified Hamiltonian expressions and the fitted molecular parameters will be presented.

¹ R.N. Zare, A.L. Schmeltekopf, W.J. Harrop, and D.L. Albritton, J. Mol. Spec. **46**, 37 (1973).

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TE'02 15 min 3:47

FIRST HIGH RESOLUTION SPECTROSCOPIC STUDY OF THE X $^2\Pi_{\Omega}$ ELECTRONIC STATE OF HI^+ : FINE AND HYPERFINE STRUCTURE ANALYSIS OF THE VIBRATION-ROTATION SPECTRUM, A. CHANDA, W.C. HO, F.W. DALBY and I. OZIER

Prior to this investigation, the spectroscopic information on HI^+ molecular ion was limited to that obtained from low resolution work using photoelectron techniques. A vibration-rotation study has now been carried out of the X $^2\Pi_{\Omega}$ electronic state of HI^+ in an a.c. glow discharge using a diode laser spectrometer with velocity modulation. A total of more than 100 transitions belonging to the ($v' \leftarrow v''$) = ($1 \leftarrow 0$) and ($2 \leftarrow 1$) vibrational bands of the $^2\Pi_{3/2}$ spin substate and to the ($1 \leftarrow 0$) vibrational band of the $^2\Pi_{1/2}$ spin substate have been recorded in the frequency range from 1990 cm^{-1} to 2260 cm^{-1} for J up to 15.5. At an estimated rotational temperature of the discharge of about 700 K, the observed full width at half maximum was 0.004 cm^{-1} . Large hyperfine splittings arising from magnetic dipole and electric quadrupole interactions have been observed for low J transitions belonging to both of the Ω substates. Precise values of hyperfine and fine structure constants as well as the vibrational and rotational constants were obtained. Preliminary values for the most important constants are listed below.

Vibration-rotation constants :

$$\begin{aligned}\omega_e &= 2195.2425(19)\text{ cm}^{-1}, & B_e &= 6.33077(69)\text{ cm}^{-1}, & p_e &= 3.5202(40)\text{ cm}^{-1}, & q_e &= -0.0038(10)\text{ cm}^{-1} \\ \omega_e\sigma_e &= 39.5970(10)\text{ cm}^{-1}, & \alpha_B &= 0.17540(43)\text{ cm}^{-1}, & \alpha_p &= 0.0498(23)\text{ cm}^{-1}\end{aligned}$$

Hyperfine coupling constants :

$$\begin{aligned}a + \frac{1}{2}(b+c) &= 0.05112(7)\text{ cm}^{-1}, & d &= 0.09945(51)\text{ cm}^{-1} \\ a - \frac{1}{2}(b+c) &= 0.09383(96)\text{ cm}^{-1}, & eQq_0 &= -0.02377(57)\text{ cm}^{-1}\end{aligned}$$

Details of the experiment and the fitted molecular parameters will be presented.

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TE'03 15 min 4:04

INFRARED ABSORPTION SPECTROSCOPY OF JET-COOLED MOLECULAR IONS

MASARU FUKUSHIMA, MAN-CHOR CHAN, YUNJIE XU, AMINE TALEB-BENDIAB, AND TAKAYOSHI AMANO

Protonated molecular ions H_3^+ , HN_2^+ , and H_3O^+ generated in a "hollow-cathode" type discharge jet have recently been studied using infrared absorption spectroscopy. The rotational temperatures of these ions in the ground state were determined to be 120 ± 20 K, 273 ± 20 K and 150 ± 20 K for H_3^+ , HN_2^+ , and H_3O^+ , respectively. This observation suggests different dynamics of ion formation under jet-expansion compared to usual hollow-cathode discharge cells, in which the rotational temperatures of the ions are determined by the temperature of the coolant.¹ The spectral linewidths and the concentrations of the ions at different positions of the jet stream will also be discussed to shed light on the dynamic characteristics of the hollow-cathode discharge jet.

¹T. Amano, J. Chem. Phys. **92**, 6492 (1990).

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TE'04 10 min 4:21

NEAR-INFRARED DIODE LASER ABSORPTION SPECTROSCOPY OF THE JET-COOLED N_2^+ ION

KENSUKE HARADA AND TAKEHIKO TANAKA

The absorption spectrum of the (2, 0) vibrational band of the $A^2\Pi_u \rightarrow X^2\Sigma_g^+$ system of the nitrogen molecular ion generated by discharge in the pulsed supersonic jet expansion has been observed by near-infrared diode laser spectroscopy. Signal-to-noise ratio greater than 40 at an effective time constant of 0.1 sec was obtained using the discharge modulation technique followed by dual-gated integration synchronous with a pulsed nozzle. The rotational temperature of the N_2^+ ion was typically 50 K in the discharge plasma in the pulsed supersonic jet expansion.

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TE'05

15 min

4:33

Carbo-ion spectroscopy with tunable diode lasers: The bending vibrations of CH_3^+

Sangwoo Joo, Frank Kühnemann^{1a}, and Takeshi Oka

The methyl cation CH_3^+ is one of the most fundamental carbo-ions which plays an important role in many fields. According to ab-initio calculations^{1,2,3} and photoelectron spectra⁴, the band origins of its two bending vibrations, ν_2 (the out of plane bending vibration) and ν_4 (degenerate bending vibration) have been predicted to be between 1350 and 1400 cm^{-1} . The theoretical studies show that the vibrational frequencies of ν_2 (parallel band) and ν_4 (perpendicular band) are very close to each other with a difference of 1-20 cm^{-1} and a strong Coriolis interaction between the two vibrational states are expected. The perturbation treatment of the vibration-rotation hamiltonian is no longer applicable.

We present the first high resolution spectra of CH_3^+ in the bending vibration frequency region at 7-8 μm . The ion was produced in a liq- N_2 cooled 6 kHz ac glow discharge with a gas mixture of 0.1: 0.1: 7.0 torr of CH_4 : H_2 : He. Velocity modulation is used in order to discriminate ion signal. 22 spectral lines have been observed. The limitation of mode coverage, large rotational constant of CH_3^+ ($B_0 = 9.36 \text{ cm}^{-1}$) and strong Coriolis interaction make the analysis difficult. If successful, the analysis will provide better understanding of vibration-rotation interaction in the molecule. Our observation will also provide a vehicle for the astronomical observation of CH_3^+ through the 8.5 μm window.

1. D.J DeFrees and A.D. McLean, J. Chem. Phys. **82**, 333 (1985)

2. P. Botschwina, in Ion and Cluster Ion Spectroscopy and Structure, edited by J.P. Maier (Elvier, Amsterdam, 1989)

3. W.P. Kraemer and V. Spirko, J. Molec. Spec. **149**, 235(1991)

4. J. Dyke, N. Jonathan, E. Lee and A. Morris, J. Chem. Soc. Faraday Trans. 2 **72**, 1385 (1976)

1a. Feodor Lynen Fellow (Alexander von Humbolt Foundation).

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TE'06

15 min

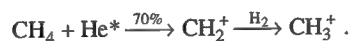
4:50

INFRARED STUDIES OF THE ν_3 BAND OF CH_2^+

Charles Gabrys, Dairene Uy, Mary-Frances Jagod, and Takeshi Oka

The spectrum of the CH_2^+ ion is difficult to analyze because of the existence of the Renner-Teller effect and a low barrier to linearity. In our previous study¹ of the ν_3 band of CH_2^+ , we could assign only 18 lines in the $K_a = 0$ series of the a -type parallel transition because of the irregularity of other series and because of the complexity of the overall spectrum due to other carbocations in the plasma.

In order to maximize CH_2^+ signals as opposed to those of CH_3^+ , we chose a plasma similar to the one in our initial scan but without H_2 since



We found that a mixture of $\text{CH}_4/\text{He} = 90 \text{ mT}/7 \text{ Torr}$ in a liquid- N_2 cooled positive column clearly distinguishes the object of our quest. An extensive scan around the band origin of $\nu_3 = 3131 \text{ cm}^{-1}$ using such conditions allowed us to unambiguously assign the two series for $K_a = 1$ and some more lines with $K_a = 2$. The series are quite irregular because of the Renner-Teller perturbation in the ν_3 state, but the ground state combination differences are fairly regular. Altogether, 45 transitions have been assigned, and 15 combination differences in the ground state have been fitted.

¹M. Rösslein, C. M. Gabrys, M.-F. Jagod, and T. Oka, J. Mol. Spectrosc. **153**, 738-740 (1992)

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TE'07 15 min 5:07

MILLIMETER-WAVE LABORATORY DETECTION OF H_2COH^+

D. Chomiak, A. Taleb-Bendiab, S. Civiš, and T. Amano

The ground state rotational spectrum of protonated formaldehyde, H_2COH^+ , has been identified and assigned following the infrared detection by Amano and Warner¹, using a magnetically confined extended negative glow discharge as a production source. The molecular constants have been determined more accurately. These parameters provide the pure rotational transition frequencies which are accurate enough for radio astronomical searches for this ion in interstellar molecular clouds.

1. T. Amano and H. E. Warner, *Astrophys. J.* **342**, L99 (1989).

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TE'08 15 min 5:24

MEASUREMENT BY MILLIMETER-WAVE SPECTROSCOPY OF TUNNELING SPLITTING FOR THE NON-CLASSICAL FORM OF C_2H_3^+ , M. BOGEY, M. CORDONNIER, C. DEMUYNCK AND J.L. DESTOMBES

The non-classical form (bridged) of the protonated acetylene C_2H_3^+ has now been identified both by IR (1) and MW (2) spectroscopy. The analysis of the ν_6 vibrational state led to the evidence of the exchange of the three protons in a tunneling rearrangement of this structure through its classical isomer (1). We report our observation of the splittings of the A-E energy levels in the ground state using millimeter wave spectroscopy.

Recent improvements of our spectrometer have increased its performance. We are now able to measure accurately the splitting of the $11_0 \leftarrow 10_1$ and $31_2 \leftarrow 30_3$ transitions. The obtained values are within the predictions of Escribano with a barrier of about 1600 cm^{-1} (3). However, up to now, the theoretical model does not fit precisely to the experimental data.

(1) M.W. Crofton, M.F. Jagod, B.D. Rehfuss and T. Oka, *J. Chem. Phys.* **91**, 5139 (1989).

(2) M. Bogey, M. Cordonnier, C. Demuynck and J.L. Destombes, *Astrophys. J.* **399**, 103 (1992).

(3) R. Escribano, private communication (1993)

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TF01 15 min 1:30

OBSERVATION OF INTERVALENCE TRANSITIONS OF NAPHTHALENE CLUSTERS AND THEIR CATIONS BY PHOTODISSOCIATION SPECTROSCOPY, HIROYUKI SAIGUSA AND E. C. LIM

We have observed intervalence transitions of the neutral and cationic clusters of naphthalene by fluorescence- and ionization-detected photodepletion spectroscopies. Upon excitation of the neutral clusters ($N=2-4$) into the S_1 state, they undergo excimer formation and absorb strongly in the 500-900-nm region, centered at 750 nm. This broad absorption band is assigned to an intervalence transition band of a strongly bound dimer core (excimer) produced in these clusters. In contrast, two absorption maxima have been observed for the corresponding cationic clusters ($N=2-7$). We attribute the one appearing at $\sim 1 \mu$ to an intervalence transition and the other at ~ 560 nm to a locally excited state which correlates to the ${}^2B_{3g}$ (D_2) excited state of the naphthalene cation. Photodissociation dynamics via the intervalence transitions will be discussed for the neutral and cationic clusters.

I. H. Saigusa, S. Sun, and E. C. Lim, J. Phys. Chem. **96**, 10099 (1992).

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TF02 15 min 1:47

SPECTRAL HOLE BURNING AS PROBE OF INTERMOLECULAR VIBRATIONS IN HYDROGEN BONDED MOLECULAR COMPLEXES

M. SCHMITT, H. MÜLLER, K. KLEINERMANN

Several hydrogen bonded clusters of phenol with water, methanol and phenol were examined by spectral hole burning (SHB). The ground state is depopulated persistently on the time scale of the experiment by a tunable dye laser (burn laser). After a variable time delay (400 to 800 ns) the population of the ground state level is probed by a second dye laser. If probe and burn laser share a common ground state level, the fluorescence caused by the probe laser is decreased [1]. Because of cluster and state selectivity of spectral hole burning, several intermolecular vibrations of Phenol-(H_2O)₃ could be assigned for the first time [2]. In opposite to Resonance Enhanced Multiphoton Ionisation with time of flight detection (REMPI-TOF) fragmentation of the clusters does not perturb the spectrum. Different conformers of one cluster size can be distinguished by SHB. The phenol dimer provides an interesting example of a cluster with two closely neighbouring electronically excited states. These excited states belong to the donor and the acceptor chromophore respectively. Spectral hole burning provides new insights in the vibrational structure of this cluster and in dynamic processes between the different potential surfaces.

[1] S.A. Wittmeyer, M.R. Topp, Chem. Phys. Lett. **163**, 261 (1989)

[2] M. Schmitt, H. Müller, K. Kleinermanns, Chem. Phys. Lett. accepted for publication (1994)

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TF03 15 min 2:04

ZEKE SPECTROSCOPIC STUDIES OF HYDROGEN-BONDED PHENOL COMPLEXES
Timothy G. WRIGHT, Otto DOPFER, Eric CORDES, Gerhard LEMBACH and Klaus MÜLLER-DETHLEFS

Phenol-X complexes ($X = \text{H}_2\text{O}$, CH_3OH , $\text{CH}_3\text{CH}_2\text{OH}$, $\text{C}_6\text{H}_5\text{OH}$ and CH_3OCH_3) have been studied using the technique of ZEKE Spectroscopy¹. Intermolecular modes of the complex cations have been obtained and in all but one of the cases, all six intermolecular modes of the cation have been observed. All spectra were obtained *via* vibronic levels in the S_1 state, and large variations in ZEKE spectral intensities were noted for different levels. Ionization energies have been obtained accurate to $\pm 5 \text{ cm}^{-1}$ and hence the increases in the strength of intermolecular bonding upon ionization could be obtained. Some qualitative trends in the latter values will be discussed.

1. T.G. Wright, E. Cordes, O. Dopfer and K. Müller-Dethlefs, J. Chem. Soc. Faraday Trans., **89**, 1609 (1993); K. Müller-Dethlefs, O. Dopfer and T.G. Wright, Chem. Rev. in press (1994).

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TF04 15 min 2:21

EMISSION FROM THE PRODUCTS OF THE MULTIPHOTON DISSOCIATION OF KETENE AND ACETYL BROMIDE, Z. LI, T.S. DIBBLE, Y. SU, J.S. FRANCISCO, M.M. MARICQ, AND J.J. SZENTE.

Multiphoton excitation of ketene, CH_2CO , with 193 nm radiation produces intense fluorescence from the $A \rightarrow X$ and $B \rightarrow X$ transitions of CH radical. Weaker emission is observed with use of 308 nm radiation. Infrared multiphoton dissociation of acetylbromide, $\text{CH}_3\text{C(O)Br}$, produces luminescence very similar to that arising from ketene. These observations represent one of few cases of observation of ultraviolet emission following infrared multiphoton excitation of a ground state species, and supports a previous suggestion of a ketene intermediate in acetylbromide dissociation.

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TF05 15 min 2:38

HIGH RESOLUTION, ROTATIONALLY RESOLVED ELECTRONIC SPECTRA OF CaC_5H_5 .

TIMOTHY M. CERNY, JAMES M. WILLIAMSON AND TERRY A. MILLER

High resolution, rotationally resolved spectra have been acquired and analyzed for both spin orbit components of the 0_0^0 and 4_0^1 bands in the $\tilde{A}^2E \leftarrow \tilde{X}^2A_1$ transition of CaC_5H_5 . The free radical CaC_5H_5 was generated by laser ablation of a Ca rod in a supersonic free jet expansion seeded with cyclopentadiene. Analysis is consistent with the proposed C_{5v} geometry of a Ca atom centered over the C_5H_5 ring.^{1,2} The fitted rotational constants can be used to estimate the $\text{Ca}/\text{C}_5\text{H}_5$ distance to be 2.33 Å in the ground state. The excited state $\text{Ca}/\text{C}_5\text{H}_5$ distance shortens by .060 Å as suggested by earlier Franck-Condon analysis.¹ The electronic orbital angular momentum is largely unquenched and no Jahn-Teller activity could be measured. Details of the analysis, interpretation of the fitted constants and their implications for other metal-cyclopentadienyl such as MgC_5H_5 will be presented.

¹ E.S.J. Robles, A. M. Ellis and T. A. Miller, *J. Am. Chem. Soc.* **114**, 7171 (1992).

² L.C. O'Brien and P. F. Bernath, *J. Am. Chem. Soc.* **108**, 5017 (1986).

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TF06 15 min 2:55

METHANE VAN DER WAALS COMPLEXES OF THE FLUORONAPHTHALENES. A PERTURBED SPHERICAL TOP ATTACHED TO A SURFACE,¹ J. F. PFANSTIEL, B. B. CHAMPAGNE, AND D. W. PRATT

We have obtained high resolution spectra of the 0_0^0 bands of the $S_1 \leftarrow S_0$ electronic transitions of methane van der Waals complexes of 1- and 2-fluoronaphthalene (1/2 FN). Each spectrum exhibits three closely spaced rotationally resolved bands, each of which has been fit to a rigid rotor Hamiltonian. Center-of-mass coordinates of CH_4 in the inertial frames of 1/2 FN have been determined using Kraitchman's equations. These coordinates are virtually the same as those for argon in the corresponding Ar-1/2 FN complexes, in all bands. The corresponding bands of Ar-1/2 FN are not split into three components. For these reasons, we believe that the three bands in CH_4 -1/2 FN are not due to different isomers, but rather are caused by the (perturbed) nearly free rotation of the attached methane. The observed intensity ratio of the bands, 5:9:10, is consistent with that expected from nuclear spin state statistics, owing to the exchange of the four equivalent hydrogen atoms. A model calculation, based on a pair potential that is slightly different in the two electronic states of 1/2 FN (the "surface" to which CH_4 is attached), reproduces the observed splitting of the bands. This calculation suggests that the rotation of CH_4 is nearly free about a C_3 axis and more strongly hindered about perpendicular axes; i.e., that the CH_4 is "bound" to the surface by a single $\text{C-H}\cdots(1/2 \text{ FN})$ bond.

1. Supported by NSF (CHE-9224398) and AFOSR (MRC-910441).

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INTERMISSION

TF07 15 min 3:30

METHYL INTERNAL ROTATION IN THE S_1 STATE OF 2-CHLORO-6-FLUOROTOLUENE: EXPERIMENT AND THEORY, E. C. Richard, R. A. Walker, K-T. Lu, and J. C. Weisshaar

Using resonant two photon ionization we have measured the low frequency torsional vibrational structure of 2-chloro-6-fluorotoluene in a skimmed molecular beam. The $S_1 \leftarrow S_0$ origin occurs at 37036 cm^{-1} (adiabatic I.P. = $9.127 \pm 0.006 \text{ eV}$). The spectrum has considerable low frequency vibrational activity with many vibrational bands ($< 500 \text{ cm}^{-1}$) showing relatively large intensities. Using a threefold symmetric potential we are able to assign the low lying torsional states of the methyl rotor ($|V_3| \sim 140 \text{ cm}^{-1}$). *Ab-initio* calculations predict a large barrier to internal rotation in S_0 ($|V_3| \sim 230 \text{ cm}^{-1}$) with the most stable confirmation having one C-H bond eclipsed with the C-F bond. In contrast to the monosubstituted *ortho* toluene derivatives the S_1 barrier to methyl internal rotation in 2-chloro-6-fluorotoluene remains relatively large. The present study extends our examination of the nature of hyperconjugative interactions involving electron donation from the n_X ($X = \text{Cl, F}$) p-type orbitals into the σ^*_{CH} orbitals of the methyl group. The analysis of both ^{35}Cl and ^{37}Cl systems will be presented.

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TF08 15 min 3:47

LOW ENERGY INTERNAL ROTATION IN THE S_1 AND GROUND CATION STATES OF 2,6-DIFLUOROTOLUENE

R. A. Walker, E. C. Richard, K-T. Lu, J. C. Weisshaar

Employing techniques of resonance enhanced two photon ionization and threshold electron pulsed field ionization, we have measured both the $S_1 \leftarrow S_0$ and cation $\leftarrow S_1$ spectra of 2,6-difluorotoluene (DFT).¹ DFT's $S_1 \leftarrow S_0$ origin lies at $37948 \text{ cm}^{-1} (\pm 0.3 \text{ cm}^{-1})$, and DFT shows an adiabatic ionization potential of $73673 \text{ cm}^{-1} (\pm 7.0 \text{ cm}^{-1})$. Slightly to higher energy of the S_1 and cation origins, we observe a number of bands which we assign to internal rotation of the DFT methyl group. Fitting these features to a sixfold symmetric potential ($\frac{V_6}{2}(1 - \cos 6\alpha)$) suggests a very low barrier to methyl rotation in both the S_1 ($|V_6(S_1)| \sim 20 \text{ cm}^{-1}$) state and cation ground state ($|V_6(D_0)| \sim 10 \text{ cm}^{-1}$). These measured barriers are consistent with *ab initio* calculations predicting a small V_6 in the ground state of DFT ($V_6(S_0) = 17.4 \text{ cm}^{-1}$). This talk will focus on the origin of these small V_6 terms in the context of V_6 potentials found for other six-fold symmetric molecules. Additionally, a coupling mechanism invoked to explain several nominally forbidden transitions observed in the spectra will be discussed.

1. R. A. Walker, E. C. Richard, K-T. Lu, J. C. Weisshaar, work in progress.

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TF09 15 min 4:04

FAR-INFRARED SPECTRA AND TWO-DIMENSIONAL POTENTIAL ENERGY SURFACES FOR THE OUT-OF-PLANE RING VIBRATIONS OF CYCLOPENTANONE IN ITS S_0 AND $S_1(n,\pi^*)$ ELECTRONIC STATES, JAEBUM CHOO AND JAAN LAANE

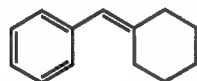
The far-infrared spectra of cyclopentanone has been reexamined. In addition to the ring bending series previously observed in the $80\text{-}100\text{ cm}^{-1}$ region, ring-twisting bands ($200\text{-}240\text{ cm}^{-1}$), bend-twist sum bands ($305\text{-}335\text{ cm}^{-1}$), and bend-twist difference bands were also detected for the first time. From this data a two-dimensional potential energy surface with a barrier to planarity of 1408 cm^{-1} and a barrier to pseudorotation of 1358 cm^{-1} was determined. This same surface yields calculated frequencies in good agreement for not only the undeuterated cyclopentanone, but also for four isotopomers. In addition to determining the potential energy surface for the S_0 electronic ground state, we have also utilized our previously reported fluorescence excitation spectra to determine the corresponding potential energy surface for the $S_1(n,\pi^*)$ electronic excited state. The barrier to planarity in the S_1 state is 1273 cm^{-1} while the barrier to pseudorotation has been reduced substantially to 850 cm^{-1} .

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TF10 15 min 4:21

SPECTROSCOPY AND CONFORMATION OF A SERIES OF BENZYLIDENE CYCLOALKANES, I.R. CABLE, N. WESTRICK, V. MANEA

Electronic spectra were recorded in a series of jet-cooled benzylidene cycloalkanes where the cycloalkane was varied in size from cyclobutane to cyclohexane (illustrated below) in order to alter the magnitude of



the steric interaction between the two rings. All spectra displayed extended low-frequency progressions which have been assigned to the torsional motion of the phenyl ring, thereby indicating that considerable change in the torsional geometry occurs following excitation to the lowest lying singlet excited state. Analysis of the level spacings leads to a detailed picture of the excited state torsional potential energy surfaces and a value for the equilibrium torsional angles in the ground electronic state. The experimentally derived ground state conformations are compared with those predicted by several different levels of theoretical calculations.

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TF11 15 min 4:38

AN AB-INITIO CALCULATION OF THE $S_0 \rightarrow S_1$ TRANSITION OF ANTHRACENE AND ITS VIBRONIC STRUCTURE, Y. HAAS, S. ZILBERG, U. SAMUNI AND R. FRANKEL.

An *ab-initio* calculation of the energy, geometry and vibrational frequencies of the $S_1(^1B_m)$ state of anthracene was performed at the UHF level, using a 3-21G basis set. The calculated 0,0 transition is at 28346 cm^{-1} (experimental 27695 cm^{-1}), the geometry is planar, with some small changes in the bond lengths. The vibrational analysis resolves some remaining uncertainties in the assignment of jet and matrix isolation fluorescence excitation spectra. In particular, bands observed at 230, 541 and 748 cm^{-1} in the jet, have no clear counterpart in the matrix. They also exhibit anomalously long radiative lifetimes. It is proposed to assign the b_{3g} symmetry modes, implying vibronic (Herzberg-Teller) coupling the a $^1B_{1u}^+$, involves excitation into a σ^* orbital.

R. Fraenkel, U. Samuni, Y. Haas and B. Dick, Chem. Phys. Lett. 203 523 (1993)

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TF12 10 min 4:55

SUPERSONIC JET SPECTRA OF PARA SUBSTITUTED ANILINES

S. WATEGAONKAR AND S. DORAISWAMY

Laser induced fluorescence spectra of the molecules 4-aminophenol ($\text{NH}_2\text{C}_6\text{H}_4\text{OH}$), anisidine ($\text{NH}_2\text{C}_6\text{H}_4\text{OCH}_3$) and phenetidine ($\text{NH}_2\text{C}_6\text{H}_4\text{OC}_2\text{H}_5$) both in excitation and emission have been observed for the first time and prominent vibronic transitions in the first 1200 cm^{-1} have been assigned. Results will be presented and discussed.

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TF13 15 min 5:07

FLUORESCENCE SPECTRA AND TORSIONAL POTENTIAL FUNCTIONS FOR *TRANS*-STILBENE IN ITS S_0 AND $S_1(\pi, \pi^*)$ ELECTRONIC STATES, WHE-YI CHIANG AND JAAN LAANE

The fluorescence excitation spectra and dispersed fluorescence spectra of *trans*-stilbene have been recorded and analyzed. Vibrational assignments for the eight low-frequency modes have been made for both the S_0 and $S_1(\pi, \pi^*)$ electronic states, and these differ substantially from those of previous workers. Two-dimensional kinetic and potential energy calculations were carried out in order to determine the potential energy surfaces for the two phenyl internal rotations, ν_{37} and ν_{48} . The function $V(\phi_1, \phi_2) = \frac{1}{2}V_2(2 + \cos 2\phi_1 + \cos 2\phi_2) + V_{12}\cos 2\phi_1\cos 2\phi_2 + V'_{12}\sin 2\phi_1\sin 2\phi_2$, with $V_2 = 1550 \text{ cm}^{-1}$, $V_{12} = 337.5 \text{ cm}^{-1}$ and $V'_{12} = 402.5 \text{ cm}^{-1}$ for the S_0 state and with $V_2 = 1500 \text{ cm}^{-1}$, $V_{12} = -85 \text{ cm}^{-1}$, and $V'_{12} = -55 \text{ cm}^{-1}$ for the $S_1(\pi, \pi^*)$ state fits the observed data (nine frequencies for S_0 , six for S_1) extremely well. The fundamental frequencies for these torsions are $\nu_{37} = 9 \text{ cm}^{-1}$ and $\nu_{48} = 118 \text{ cm}^{-1}$ for the S_0 state and $\nu_{37} = 35 \text{ cm}^{-1}$ and $\nu_{48} = 110 \text{ cm}^{-1}$ for the S_1 excited state. The third torsion, the internal rotation about the C=C bond, was assigned at 101 cm^{-1} for the S_0 state based on a series of overtone frequencies. For S_1 , $\nu_{35} = 99 \text{ cm}^{-1}$ based on observed frequencies at 198, 396 cm^{-1} , etc. A one-dimensional potential energy function of the form $V(\theta) = \frac{1}{2}V_1(1 - \cos \theta) + \frac{1}{2}V_2(1 - \cos 2\theta) + \frac{1}{2}V_4(1 - \cos 4\theta)$ was utilized to reproduce the frequencies for the ground state. For the excited state an additional V_8 term was added in order to fit the data for the *trans* potential energy well. The data indicate that the *trans* \rightarrow twist barrier for the S_1 state is higher than 1400 cm^{-1} .

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TF14 15 min 5:24

TRIPLET STATE ELECTRONIC STRUCTURE OF ZINC (II) TETRAPHENYLPORPHYRINS, V.A. WALTERS, J.C. DE PAULA, B. JACKSON, C. NUTAITIS, K. HALL, J. LIND, K. CARDOZO, K. CHANDRAN, D. RAIBLE, AND C.M. PHILLIPS

The effects of meso-substitution and axial ligation on the energies of two triplet states of a series of zinc (II) tetraphenylporphyrins (ZnTPPs) have been investigated using a combination of phosphorescence and triplet-triplet absorption spectroscopy. For both the lowest energy triplet state (the T_1 state) and a higher energy triplet state, the pattern of energy shifts was primarily in accord with the electron-donating or electron-withdrawing nature of the meso-substituent. However, the magnitude of the energy shifts due to meso-substitution was found to be significantly greater for the higher energy state. Axial ligation had a similar effect on the energies of both states. These observations will be discussed in relation to results obtained previously from transient resonance Raman spectroscopy of the lowest triplet states of tetraphenylporphyrins.

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TG01 10 min 1:30

GROUND STATE OF THE NbH_2 MOLECULE IN RARE GAS AND DEUTERIUM MATRICES, R.J. VAN ZEE, S. LI, AND W. WELTNER, JR.

Hyperfine splittings in the electron-spin-resonance spectra of ^{93}Nb atoms + H_2/D_2 in argon, krypton, and deuterium matrices at 2-4K indicate that the $\text{NbH}_2/\text{NbD}_2$ molecule is being observed. However, the spectra indicate that the molecule has a doublet ground state, and if bent, it must be rotating in the solids. Theory¹ favors a $^4\text{B}_1$ ground state. The hyperfine splittings and g values will be discussed in terms of molecular structure and bonding.

1. K. Balasubramanian and Ch. Ravimohan, J. Phys. Chem. **93**, 4490 (1989).

Address of Van Zee, Li, and Weltner: Department of Chemistry, University of Florida, Gainesville, FL 32611-2046.

TG02 10 min 1:42

INFRARED SPECTRA OF Si_2 , Ge_2 , Sn_2 , SiGe , and SiSn MOLECULES IN RARE-GAS MATRICES: ELECTRONIC TRANSITIONS AND MAGNETIC EFFECTS, S. LI, R.J. VAN ZEE, AND W. WELTNER, JR.

Absorption spectra of these molecules, observed between 200 and 4800 cm^{-1} in neon and argon matrices at 4K were assigned to the lowest $^3\Pi - X^3\Sigma^-$ electronic transition.¹ In all five cases, the Franck-Condon envelope of vibrational bands allowed T_{00} , ω_e' , $\omega_e'x_e'$ to be determined. A Zeeman effect on this transition was detected in magnetic fields up to 4T. The transition from case (a) to case (c) is considered as the spin-orbit coupling increases from Si_2 to Sn_2 .

1. T.N. Kitsopoulos, C.J. Chick, Y. Chao, D.M. Neumark, J. Chem. Phys. **95**, 1441 (1991); C.W. Bauschlicher, Jr. and S.R. Langhoff, J. Chem. Phys. **87**, 2919 (1987); K. Balasubramanian, J. Mol. Spectr. **123**, 228 (1987); F.L. Sefyani, J. Schamps, and J.M. DeLaval, J. Mol. Spectr. **162**, 269 (1993).

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TG03 15 min 1:54

REACTIONS OF LASER ABLATED Ti ATOMS WITH HYDROGEN DURING CONDENSATION IN EXCESS ARGON. INFRARED SPECTRA OF THE TiH, TiH₂, TiH₃ AND TiH₄ MOLECULES, George V. Chertihin and Lester Andrews

Reactions of pulsed-laser evaporated Ti atoms with H₂ in a condensing argon stream gave TiH, TiH₂, TiH₃, TiH₄ and polymeric species. The main difference between pulsed laser and thermal evaporation Ti atom reactions is the observation of all four products directly after sample deposition and the appearance of the new TiH and TiH₃ radicals with laser evaporation. The assignments were based on concentration dependence and isotopic substitution and were confirmed by SCF frequency calculations. The stable D_{3h} titanium trihydride radical was identified from agreement between calculated and observed values for the 8 active stretching frequencies for TiH₃, TiH₂D, TiHD₂ and TiD₃. Both experimental and theoretical results show that reactions with H atoms play an important role in the reaction mechanism.

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TG04 15 min 2:11

REACTIONS OF LASER ABLATED BE ATOMS WITH O₂: INFRARED SPECTRA OF BERYLLIUM OXIDES IN SOLID ARGON, Craig A. Thompson and Lester Andrews

Pulsed-laser ablated beryllium atoms codeposited with O₂ in excess argon at 10K yielded new beryllium-oxygen molecules. The initial reaction to make BeO is endothermic, but activation energy is provided by hyperthermal Be atoms. A strong band at 1572.9 cm⁻¹ and weak band at 398.9 cm⁻¹ gave oxygen isotopic shifts consistent with a BeO diatomic molecule and are assigned to the O₂-BeO complex analogous to the Ar-BeO complex. A sharp band at 1413.2 cm⁻¹ exhibited an oxygen isotopic triplet with ^{16,18}O₂ and shifts appropriate for linear OBeO. A nearly coincident band at 1412.4 cm⁻¹ gave an isotopic doublet and shifted in agreement with linear BeOBe. Quantum chemical calculations at the MBPT[2] level predict ³Σ ground states and ν₃ fundamentals at 1422.5 and 1418.2 cm⁻¹ for OBeO and BeOBe, respectively, in excellent agreement with the observed values. Three bands at 1131.2, 866.3, and 522.4 cm⁻¹ increased together on photolysis, yielded isotopic triplets, and agreed with MBPT[2] calculations for rhombic Be₂O₂. A sharp photosensitive band at 988.6 cm⁻¹ gave oxygen isotopic shifts consistent with another linear OBeO species and is tentatively assigned to the molecular anion. An intense band at 1465.1 cm⁻¹ that appeared on annealing gave oxygen isotopic shifts in agreement with calculations for linear BeOBeO. Two bands at 1288.9 and 1264.1 cm⁻¹ appeared on photolysis and gave isotopic triplets and shifts that are in excellent agreement with calculations for branched BeBeO₂. Annealing produced bands at 871.8 and 436.1 cm⁻¹ that decreased on photolysis and are assigned to BeO₃.

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TG05 15 min 2:28

Pulsed-Laser Evaporated Magnesium Atom Reactions with Hydrogen: Infrared Spectra of Five Magnesium Hydride Product Molecules, Thomas J. Tague Jr. and Lester Andrews

Pulsed-laser ablated magnesium atoms have been codeposited with mixtures of hydrogen and argon onto a 10 K substrate. Assignments to product molecules have been made on the basis of broadband photolysis and annealing behavior, deuterium and ^{26}Mg isotopic substitution, and *ab initio* calculations. The predominant reaction products are MgH (infrared absorption at 1422.1 cm^{-1}) and linear MgH_2 ($\nu_3=1571.0$ and $\nu_2=439.8\text{ cm}^{-1}$). Absorptions attributed to the two lowest energy MgH dimers HMgMgH (1491.8 cm^{-1}) and the rhombic dimer $(\text{MgH})_2$ (1022.8 and 605.4 cm^{-1}) are evident as well as the bridged MgH_2 dimer $\text{HMg}(\text{H})_2\text{MgH}$ (1531.0 , 1164.2 , 1013.7 , and 613.9 cm^{-1}). An increase of HMgMgH and $(\text{MgH})_2$ dimer formation on photolysis indicates photoactivation of Mg_2 , allowing reaction with H_2 . Annealing of the matrix yielded little increase in dimer formation, which indicates limited mobility of magnesium hydrides in the matrix. However, H_2 complexes with both MgH and MgH_2 increase on annealing.

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Address of Andrews: Department of Chemistry, University of Virginia, Charlottesville, VA 22901.

TG06 15 min 2:45

FTIR OBSERVATION OF VIBRATIONAL FUNDAMENTALS FOR SMALL SILICON CLUSTERS TRAPPED IN SOLID ARGON, SHUNLIN WANG, C.M.L. RITTBY, AND W.R.M. GRAHAM

Assignments have recently been proposed for a number of symmetric vibrations of the Si_3 and Si_4 clusters based on results from experimental studies using photoelectron, threshold photodetachment,¹ and Raman² spectroscopy and from theoretical *ab initio* calculations.³

Results will be reported from a Fourier transform infrared study to observe the infrared allowed fundamentals of small silicon clusters produced by trapping the products of the laser evaporation of silicon powder in solid argon at 10 K. Measured frequencies and isotopic shifts will be compared with the results of new *ab initio* calculations carried out as part of the present investigation.

1. T.N. Kitsopoulos, C.J. Chick, A. Weaver, and D.M. Neumark, J. Chem. Phys. **93**, 6108 (1990); C.C. Arnold and D.M. Neumark, J. Chem. Phys. **99**, 3353 (1993).
2. E.C. Honea, A. Ogura, C.A. Murray, K. Raghavachari, W.O. Sprenger, M.F. Jarrold, and W.L. Brown, Nature **366**, 42 (1993).
3. C.M. Rohlffing and K. Raghavachari, J. Chem. Phys. **96**, 2114 (1992).

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TG07 15 min 3:02

PHOTOCHEMISTRY AND SPECTROSCOPY OF MATRIX ISOLATED $C_3 \cdot H_2O$ COMPLEX.
J. Szczepanski, S. Ekern and M. Vala.

Fourier transform infrared absorption measurements of Nd/YAG-laser-ablated isotopic mixtures of ^{13}C and ^{12}C isolated with water in argon matrices have revealed the existence of a complex of $^{12/13}C_3$ with water. The structure of the complex, deduced from a normal coordinate analysis of the vibrational spectrum; and from a HF/6-31G* *ab initio* calculations, will be discussed. Photolysis (405 nm) of the matrix sample leads to the disappearance of the complex bands and the formation of two conformers of 3-hydroxypropadienyldiene. The predicted structure and vibrational spectrum of these intermediates, calculated via *ab initio* theory, will be compared to experimental results.

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INTERMISSION

TG08 15 min 3:40

FTIR SPECTROSCOPY OF MASS-SELECTED, MATRIX-ISOLATED CATIONS, J. T. GODBOUT, T. M. HALASINSKI, J. ALLISON, AND G. E. LEROI

Instrumentation which allows the infrared spectroscopic observation of mass-selected, matrix-isolated ions has been developed. Mass-selected cations are generated using a modified quadrupole mass spectrometer and subsequently trapped in neon or argon matrices. Preliminary experiments with CF_3^+ , generated from CF_3X ($X = H, Cl, Br$), have shown that sufficient quantities can be isolated to permit detection of the antisymmetric stretch (ν_3). The cations are observed without the concurrent deposition of anions. Negatively charged particles are, however, observed upon warming of the substrate, indicating that the matrix is maintaining approximate electrical neutrality by an as yet unknown mechanism. Some of the small amount of neutral precursor which diffuses onto the matrix may undergo electron attachment. Absorptions consistent with previous assignments to CF_3Cl^- in argon¹ have been observed, but similar features have not yet been detected in neon.

¹Prochaska, F.T.; Andrews, L., *J. Am. Chem. Soc.* **1978**, *100*, 2102.

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TG09 15 min 3:57

ABSOLUTE INFRARED INTENSITY MEASUREMENTS FOR MATRIX-ISOLATED SAMPLES.
WILLIS B. PERSON, KRYSTYNA SZCZEPANIAK, AND JANET E. DEL BENE.

Techniques are discussed for measuring infrared intensities for samples isolated in an Argon matrix held on a cold window at 13 K in a closed cycle helium cryostat. The measurements have been calibrated by comparison with conventional gas phase studies of the absolute intensities for H₂O, pyridine, and p-quinone, among other systems. These results are then compared with results from *ab initio* quantum mechanical calculations and analyzed critically.

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TG11 15 min 4:14

**Mixing of Atomic Rydberg and Molecular Charge Transfer States of
 Fluorine Atoms in a Neon Matrix.**

C.B. Bressler, W.G. Lawrence, and N. Schwentner

The spectroscopy of fluorine atoms in a neon matrix is used to develop a model of excited state electronic guest-host coupling of F atom rydberg states and Ne⁺F⁻ charge transfer states. F atoms are produced in a matrix of original composition F₂/Ne (1/1000) by photodissociation of F₂ at 14 eV. Synchrotron radiation in the range of 60 nm to 160 nm is used to probe the molecular F₂ and atomic F concentration by fluorescence. Absorption, excitation, and emission spectra are used to characterize the excited state potentials. Excitations and emissions of both the F atom Rydberg states and the Ne⁺F⁻ charge transfer states are observed. These spectra are used to develop a configuration coordinate model of the manifold of excited states which describes the nonradiative relaxation and the observed emissions.

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 Universitat Berlin, D-14195 Berlin Germany

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TG12 15 min 4:31

Many Body Potentials of an Open Shell Atom: Spectroscopy of Spin-Orbit Transitions of Iodine in Crystalline Xe and Kr.

W.G. Lawrence, and V.A. Apkarian

Emission spectra of spin excited iodine in a crystalline Xe at 15 K, 35 K and 110 K are presented and analyzed in terms of anisotropic pair interactions. In the octahedral trapping site, the atomic 2P iodine states split into $E_{1/2}$ and $G_{3/2}$ states of the O_h double group. The fourfold degenerate $G_{3/2}$ state is subject to a strong Jahn-Teller instability and further splits by coupling to phonons into $E_{1/2}$ and $E_{3/2}$ Kramers pairs. The observed emission spectra are composed of two bands corresponding to $2E_{1/2} \rightarrow 1E_{1/2}$ and $2E_{1/2} \rightarrow 1E_{3/2}$ transitions. The isolated atom spectra are simulated by Monte Carlo methods which assume classical statistics in the heavy atom coordinates, and adiabatic following of the electronic coordinate. Minor modifications of the gas phase pair interactions, and a temperature dependent spin-orbit splitting constant adequately reproduce the experimental spectra.

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Address of Lawrence: Dept. of Chemistry, Emory University, Atlanta GA.

TG13 10 min 4:48

Morphology Effects on the Spectroscopy and Dynamics of HCl in an Argon Matrix

H.-S. Lin, W.G. Lawrence, and M.C. Heaven

The effects of the structure and form of the host argon matrix on the spectroscopy, thermal dynamics, and photodissociation dynamics of HCl are reported. Raman spectra are used to identify monomer, dimer, and higher order clusters of HCl in the matrix. Annealing the matrix at 30 K for 5 minutes shows a shift of population from monomer and low order clusters to large solid-like clusters. Models show that this process is expected to be defect driven. Laser induced fluorescence of Cl_2 and the Raman spectra are used to monitor the photodissociation of $(HCl)_n$ clusters to form Cl_2 . The formation of Cl_2 monomers from $(HCl)_2$ dimers is distinguishable from photodissociation of larger $(HCl)_n$ clusters.

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TG14 10 min 5:00

SIMULATIONS OF KRYPTON MATRIX EFFECTS ON THE ELECTRONIC SPECTRUM OF Na_2 . A.V.NEMUKHIN, B.L.GRIGORENKO, AND G.B.SERGEEV

A model has been developed to estimate inert matrix effects on spectral properties of matrix-isolated species. The approach is based on the one-electron approximation within the LCAO scheme. Conventional Hartree-Fock operator of the trapped molecule is modified by an external field created by matrix atoms. Temporary positions of all atomic centers are found with the molecular dynamic simulations carried out for particular conditions. Effective potentials from matrix atoms are constructed with the help of the density functional theory. The model has been tested for the $\text{Na}_2\text{Kr}_{62}$ system and parameters have been obtained to reproduce the known experimental findings¹, namely, the blue shift for the B-X and the red shift for the A-X transitions in Na_2 in krypton matrices at 4K compared to gas phase spectra.

1. M.Hofmann, S.Leutwyler, and W.Schulze, Chem.Phys. **40**,145 (1979)

Address of Nemukhin, Grigorenko, and Sergeev: Department of Chemistry, Moscow State University, Moscow, 119899 GSP, RUSSIA

TG15 15 min 5:12

INTERACTION OF TRAPPED H(D) ATOMS WITH Xe MATRIX INFLUENCED BY ZERO-POINT VIBRATIONS OF THE LIGHT ATOMS, YU.A.DMITRIEV

Hydrogen and deuterium atoms are stabilized in xenon matrix from the gas phase and investigated by ESR¹. It is shown that being deposited from the gas discharge in a mixture of H_2 and D_2 with xenon, H and D atoms are trapped in the substitutional position of the matrix crystal lattice.

ESR linewidths of H and D show an isotope effect, that is $(\Delta H)^H/(\Delta H)^D = 1.10(4)$, where $(\Delta H)^H$ and $(\Delta H)^D$ are the peak-to-peak linewidths for H and D atoms, respectively. The shape of the ESR lines observed is close to Gaussian. The linewidths are found to be greatly increased by the zero-point vibrations of the atoms, the dynamical broadening being nearly equal to the static one. We show that substitutional H and D atoms trapped in solid xenon perform measurably anharmonic vibrations, and the spherically symmetric potential well which is to model the actual one for the substitutional hydrogen atom has a rather flat bottom.

The coefficient $\nu(r) = \gamma \exp(-\eta r)$ (where γ and η are constants) of the transfer of the electronic charge from Xe atom to H atom in Xe-H "molecule" is estimated using the experimental data, r being the interatomic distance, $\gamma = 25.71$, $\eta = 1.25$, in atomic units.

A comparison is carried out between experimental and theoretical values for the relative matrix shift of the trapped H atom hyperfine (hf) structure constant, and it is found that experimental and theoretical quantities are in satisfactory agreement: $(\Delta A/A_f)_{\text{exp.}} = -1.05\%$, $(\Delta A/A_f)_{\text{theor.}} = -0.98\%$, where $\Delta A = A - A_f$, and A_f is the hf constant of the free atom.

1. Yu.A.Dmitriev. J.Phys.: Condens. Matter **5**, 5245(1993).

Address: A.F.Ioffe Physico-Technical Institute, St. Petersburg, 194021 Russia

TH01 20 min 1:30

RYDBERG STATES AND RYDBERG MOLECULES

G. HERZBERG

The history of Rydberg states in atoms and molecules will be briefly summarized. If the ground state of a molecular system is unstable (as for example two He atoms) while most excited states are stable Rydberg states, we may describe the system as a Rydberg molecule. The simplest diatomic example is the He₂ molecule, while the simplest polyatomic system would be the H₃ molecule discovered only in 1979. In recent years many other examples have been studied and will be briefly summarized.

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TH02 15 min 1:52

RYDBERG STATES OF THE RARE GAS DIMERS, M. GINTER

Major features of the Rydberg electronic structures and associated spectra for the rare gas dimers He₂, Ne₂, Ar₂, Kr₂ and Xe₂ are summarized. Although the ground states of these molecules have only shallow van der Waals minima, the Rydberg states built on at least the ground ionic core state, X²Σ_u⁺, have significant minima. For He₂, hundreds of these states have been observed experimentally and associated with the configurations [1σ_g²1σ_u]nℓλ. Recent spectroscopy of the heavier dimers indicate similar Rydberg structures associated with configurations in which the ionic portions (the orbitals in the square brackets) are suitably expanded. Rotationally resolved spectra for He₂, Ne₂, and Ar₂ and partially resolved data for Kr₂ and Xe₂, provide an experimental basis for structural correlations both within the homologous series and between theory and experiment. Major unsettled questions include the prospects for channel coupling between Rydberg states built on core states other than X²Σ_u⁺ with Rydberg states based on X²Σ_u⁺.

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TH03 10 min 2:09

ROTATIONAL INTERACTIONS IN THE EXCITED SINGLET UNGERADE ELECTRONIC STATES OF N₂

SIMON EDWARDS AND LYDIA TCHANG-BRILLET

The theoretical model of the ¹Σ_u⁺ and ¹Π_u Rydberg and valence states of the nitrogen molecule established by D. Stahel, M. Leoni and K. Dressler (*J. Chem. Phys.*, **79**, 2541 (1983)) has been extended to include rotationally excited energy levels. Two methods of calculation have been used to study the effects of both homogeneous and heterogeneous state mixing on individual rovibronic levels. This revised model is being used to analyse the intensity distribution observed in the high resolution vacuum ultraviolet emission spectrum of N₂. We will present details of our calculations together with some preliminary results concerning the spectral analysis.

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TH04 15 min 2:21

RYDBERG-RYDBERG EMISSION SPECTRUM OF CARBON MONOXIDE IN THE NEAR-INFRARED REGION: AN *AB INITIO* STUDY OF NEWLY OBSERVED $^3\Pi - ^3\Sigma^+$ TRANSITION, T. HIRANO, K. ISHII, Y. SHIBA, U. NAGASHIMA, K. SATO, AND K. KAWAGUCHI

Recently we have observed a new emission spectrum of carbon monoxide (CO) in the near-infrared region, 8240 cm^{-1} , which can be ascribed to the transition between $^3\Pi$ and $^3\Sigma$ states. In order to identify the states, potential energy and transition dipole moment curves for the lowest four valence ($a\ ^3\Pi$, $a'\ ^3\Sigma^+$, $d\ ^3\Delta$, and $e\ ^3\Sigma^-$) and the lowest three Rydberg ($b\ ^3\Sigma^+$, $j\ ^3\Sigma^+$, and $c\ ^3\Pi$) triplet states of CO were calculated theoretically by the highly correlated *ab initio* Multi-Configuration Self-Consistent Field and internally contracted Multi-Reference Configuration Interaction (MCSCF-MRCI) method with basis sets of double-zeta plus polarization quality.

Observed $^3\Pi - ^3\Sigma$ spectra can be assigned to none of the transitions between valence $^3\Pi$ and $^3\Sigma$ states nor to those between valence and Rydberg states. Only possibility remained is the transition between the low-lying $c\ ^3\Pi$ and $b\ ^3\Sigma^+$ Rydberg states. The potential curves for these Rydberg states are isolated clearly enough to give simple emission spectrum, and the transition dipole moment between these states is very large, 8 Debye. These indicate that the newly observed spectrum should be attributed to the transition between $c\ ^3\Pi$ and $b\ ^3\Sigma^+$ states.

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TH06 15 min 2:38

HIGH RESOLUTION PHOTOIONIZATION SPECTROSCOPY OF NO RYDBERG STATES

J.GUO, A. Mank, and J.W. Hepburn

Photoionization efficiency spectroscopy and photoelectron spectroscopy have been used to study the autoionization of NO Rydberg states. The experiment has been carried out using a rotationally cooled supersonic molecular beam of NO and coherent vacuum ultraviolet radiation generated by resonantly enhance four-wave difference frequency mixing. We have studied the NO Rydberg states in the region from $(\text{NO}^+) X^1\Sigma^+$, $v^+=0$ to $v^+=2$ ($74650\text{ cm}^{-1} - 80040\text{ cm}^{-1}$).

The rotational structure of the ns, np, nd, nf Rydberg states has been clearly observed. The broadened line profile and the perturbed positions of some Rydberg levels are evidence for Rydberg-valence interaction and Rydberg-Rydberg interaction. Parts of data have also been compared with the results of quantum defect calculation.^{1,2}

Currently, the angle-resolved photoelectron spectra of specific Rydberg states are being recorded to study the branching ratios of different vibration decay channel and the asymmetry parameter for each vibrational decay channel, which is important for understanding the autoionization of NO Rydberg states

1) A.Giusti-Suzor and Ch.Jungen, *J.Chem.Phys.* **80**, 986 (1984)

2) J.W.Hepburn and Ch.Jungen, unpublished

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INTERMISSION

TH07 30 min 3:15

RYDBERG STATES OF MOLECULES - AN OVERVIEW
CHRISTIAN JUNGEN

In recent years the field of Rydberg spectroscopy and dynamics has rapidly expanded in a variety of directions. This talk presents an overview of the following aspects of the field:

- The interconversion of energy between nuclear and electronic degrees of freedom: rovibronic interactions, preionization and predissociation.
- Rydberg states of polyatomic molecules.
- High orbital angular momentum states and their role in ZEKE (zero kinetic energy electron) spectroscopy.
- Rydberg states of dipolar systems.
- Rydberg molecules.
- The role of Rydberg states in collisional processes.

The usefulness of MQDT (multichannel quantum defect theory) for the analysis of Rydberg states and dynamics will be stressed.

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TH08 15 min 3:50

**Three-Color Triple Resonance Spectroscopy of Highly Excited
 ng Rydberg States of NO.**
A. Fujii and N. Morita

Laser multiphoton ionization spectroscopy of highly excited ng Rydberg states ($n=11-67$, $v=0$ and 1) of NO was performed. Three-color triple resonance technique was used for rotationally state selective excitation of high ng Rydberg states. The observed term values were well reproduced by theoretical calculation based on the long range force model. The experimental evidence for fast autoionization decay in the ng Rydberg states, which has been theoretically predicted, was found at first. Not only autoionization, but also predissociation decay was observed.

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TH09 15 min 4:07

ROTATIONAL ANALYSIS OF THE RYDBERG STATES ($n \geq 4$, $v = 0, 1, 2$) OF CO BY TRIPLE RESONANT MULTIPHOTON SPECTROSCOPY.

T. EBATA, M. KOMATSU AND N. MIKAMI

Rotationally resolved spectra of the ns, np, nd and nf ($n \geq 4$, $v = 0 \sim 2$) Rydberg states of CO were measured by triple resonant multiphoton spectroscopy, where the $3s\sigma B^1\Sigma^+$ state was used as an intermediate state. From the analyses of the rotational structures, electronic term values, quantum defects and rotational constants were obtained for each states and their dependencies on the principle quantum number will be discussed. A long range force model was applied for the nf Rydberg states and the ionization potential, the polarizability and the quadrupole moment of the CO^+ core were obtained.

$$T_{\infty}(v=0) = 113025 \text{ cm}^{-1}, T_{\infty}(v=1) = 115209 \text{ cm}^{-1}, T_{\infty}(v=2) = 117368 \text{ cm}^{-1}$$

$$\alpha = 9 \text{ a.u.}, Q_{zz} = 0.96 \text{ a.u.}$$

Several perturbations were observed in the Rydberg states. Especially, strong mixing was found between the $ns\sigma$ and the $(n-1)d\sigma$ states. Local perturbation between the $ns\sigma$ and the $(n-1)f$ states was also observed. Most of the states are predissociative and the potential curve of the repulsive $D^1\Sigma^+$ state was determined by an analysis of the bandwidths of the $ns\sigma$ ($n = 4 \sim 6$, $v = 0, 1$) states.

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TH10 15 min 4:24

RYDBERG STATES OF B_2 BY RESONANCE ENHANCED MULTIPHOTON IONIZATION SPECTROSCOPY, RUSSELL D. JOHNSON III, KARL K. IRIKURA, and JEFFREY W. HUDGENS

Electronic transitions from the $^3\Sigma_g^-$ ground state to Rydberg states have been observed in the 280 to 380 nm region, corresponding to a two-photon energy region of 53000 to 72000 cm^{-1} . The B_2 was produced by the reaction of diborane (B_2H_6) with atomic fluorine or chlorine in a flow reactor. The B_2 was multiphoton ionized and the ions mass selected. Spectra were obtained for the $^{11}B^{11}B$ and $^{11}B^{10}B$ isotopomers.

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TH11 15 min 4:41
On the Lifetimes of Rydberg States Probed by Delayed Pulsed Field Ionization
F. Merkt and R. N. Zare

We present a simple model to evaluate the degree of l and m_l mixing in high Rydberg states that results from perturbations caused by weak, homogeneous dc electric fields and static ions. This model predicts the nature and the lifetime of these states qualitatively. The theoretical predictions are discussed in the light of recent experimental observations and explain several seemingly contradictory results obtained using zero-kinetic-energy (ZEKE) pulsed field ionization (PFI) photoelectron spectroscopy.

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TH12 15 min 4:58
RYDBERG STATE DYNAMICS OF ROTATING, VIBRATING H_3
AND THE JAHN-TELLER EFFECT, J.A. STEPHENS AND C.H. GREENE

We are developing a multichannel quantum defect formulation to describe the collision of a Rydberg or continuum electron with a vibrating and rotating polyatomic ion.¹ We formulate a full rovibronic frame transformation which accounts simultaneously for vibrationally and rotationally inelastic collisions (preionization) and ℓ uncoupling. Interactions among degenerate Rydberg series, arising from Jahn-Teller distortions of molecular geometry, play an important role in the formulation. An application to the $1s^2 3s A'_1 \rightarrow 1s^2 \epsilon p A'_2, \epsilon p E'$ Rydberg photoabsorption spectrum of H_3 accounts for many of its observed features.²

1. J. A. Stephens and C. H. Greene, Phys. Rev. Lett. **72**, 1624 (1994).
2. M. C. Bordas, L. J. Lembo, and H. Helm, Phys. Rev. A **44**, 1817 (1991).

Address of Stephens, Greene: Joint Institute for Laboratory Astrophysics and Department of Physics, University of Colorado, Boulder, CO 80309-0440.

TH13 15 min 5:15

THE 7i-6h AND 7h-6g ELECTRONIC SPECTRA OF H₂ AND THE PREDICTION OF H₂ INTER-RYDBERG EMISSION IN THE INTERSTELLAR MEDIUM.

R.I.STICKLAND, P.B.DAVIES, B.J.COTTERELL AND F.J.BASTERRECHEA

The relatively compact 7i-6h and 7h-6g inter-Rydberg spectra of H₂ were observed for the first time in a diode laser absorption experiment.¹ The spectra were assigned using the long range multipole-polarisation model of high l Rydberg states. The model is also used to predict other high l inter-Rydberg spectra with regard to possible astronomical observations; a number of objects e.g. supernova remnants and 'shocks' appear to be prime candidates.²

1. F.J.Basterrechea, P.B.Davies, D.M.Smith and R.J.Stickland, Mol.Phys., in press (1994).

2. D.Green, M. Stark, B.J.Cotterell and R.J.Stickland (in preparation).

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WA01**40 min**

SPECTROSCOPY AND DYNAMICS IN HIGHLY VIBRATIONALLY EXCITED MOLECULES.
F. FLEMING CRIM*

Highly vibrationally excited molecules, containing enough energy to overcome typical barriers to reaction, are crucial in many chemical processes. Characterizing highly vibrationally excited molecules at the level of individual quantum states allows their exploitation in detailed studies of photodissociation and bimolecular reaction. In favorable cases, a clear knowledge of the nature of the initially excited states permits the *control* of the course of a photodissociation or bimolecular reaction. The experiments described here are examples of spectroscopically *characterizing* highly vibrationally excited molecules and using their properties to *control* their chemistry.

We have used vibrational overtone excitation to prepare single quantum states in acetylene (C_2H_2) and then probe their composition using laser induced fluorescence. This approach has provided the first direct measurement of the frequencies of the *ungerade vibrations in the electronically excited state* and *identified the strongly coupled vibrational states in the ground electronic state*. These measurements go beyond characterizing the states. By preparing highly vibrationally excited states of HOD using vibrational overtone excitation, we have *controlled the breaking of a selected bond* by photodissociating the vibrationally excited molecule. Excitation from a vibrationally excited state to a dissociating electronically excited state, which we designate vibrationally mediated photodissociation, takes the system to otherwise inaccessible parts of the electronically excited potential energy surface and, hence, changes the dissociation dynamics. This approach is not limited to vibrational overtone excitation, and we have recently used stimulated Raman excitation to prepare several different vibrational states in HNCO and observe characteristically different photodissociation dynamics from each.

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WA02**40 min**

QUANTITATIVE SPECTROSCOPY WITH FOURIER TRANSFORM INSTRUMENTS, J. W. C. JOHNS.

The accuracy of measurements, particularly of intensities, using Fourier transform spectrometers has improved greatly over the last ten years. It is now possible to make intensity measurements which are reliable to about 1% which is perhaps better than actually needed by atmospheric physicists.

The process by which FT data can be reduced to intensity, lineshape and positional information will be reviewed. Particular attention will be given to measurements made at relatively long wavelengths where thermal radiation from room temperature sources must be properly accounted for.

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INTERMISSION

WA03**40 min****LABORATORY EVIDENCE FOR THE NATURE OF THE CARRIERS OF SOME DIFFUSE INTERSTELLAR BANDS**John P. MAIER

Electronic absorption spectra of highly unsaturated hydrocarbons embedded in 5 K neon matrices suggest that these species may be the carriers of some of the known diffuse interstellar bands. The laboratory data have been obtained by an approach which combines mass-spectrometry and matrix isolation techniques¹. Mass-selected species are codeposited with excess of neon on a metal surface at 5 K to form the matrix and the absorption spectra are then measured. The carbon chains C_nH_m , with $n = 6-14$ and $m < 3$, show absorption bands in the visible and near infrared regions², which lie close to the observed diffuse interstellar bands. The correspondences are particularly striking in the 700-900 nm range. Predictions for further astrophysical measurements of such bands are made.

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1. D. Forney, M. Jakobi and J.P. Maier, J. Chem. Phys., **90**, 600 (1989)
 2. J. Fulara, D. Lessen, P. Freivogel and J.P. Maier, Nature, **366**, 439 (1993)
-

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WA04**40 min**

ELECTRONIC SPECTROSCOPY AND ELECTRONIC STRUCTURE OF THE 3d TRANSITION METAL ALUMINIDES: AlCa, AlV, AlCr, AlMn, AlCo, AlNi, AlCu, AND AlZn,
JANE M. BEHM AND MICHAEL D. MORSE

A systematic study of the chemical bonding between aluminum and the 3d series of transition metal atoms has been initiated using the technique of resonant two-photon ionization spectroscopy of the diatomic metals in a jet-cooled supersonic expansion. Rotationally resolved studies have led to the determination of $^2\Pi$, $^3\Delta$, $^2\Pi$, $^1\Sigma^+$, and $^2\Pi$ ground states for AlCa, AlMn, AlCo, AlNi, AlCu, and AlZn, respectively. In addition, the observation of abrupt predissociation thresholds in the spectra of AlV, AlCr, AlCo, and AlNi has permitted the bond strengths of these transition metal aluminides to be estimated. For the transition metals which readily adopt a $3d^{n+1}4s^1$ configuration, strong bonds are found to result from the formation of a two electron $3p\sigma_{Al}-4s\sigma$ bond. This leads to bond strengths and bond lengths of 1.844 eV and 2.38 Å in AlCo; 2.29 eV and 2.32 Å in AlNi; 2.32 eV and 2.34 Å in AlCu; and a bond strength of 2.27 eV in AlCr. The transition metals which cannot readily adopt a $3d^{n+1}4s^1$ configuration are found to bond via $3p\pi$ approach of the aluminum atom to the $3d^4s^2$ metal atom, resulting in much longer bond lengths of 3.15 Å (AlCa), 2.70 Å (AlMn), and 2.69 Å (AlZn). These periodic trends will be discussed, and evidence will be presented for the existence of a $3p\pi_{Al}-3d\pi$ bonding interaction in the cases of AlMn and AlCo.

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WE01 15 min 1:30

ANALYSIS OF THE H_2^{80}Se HIGH RESOLUTION INFRARED SPECTRUM. EQUILIBRIUM STRUCTURE

J.-M. FLAUD, PH. ARCAS, C. CAMY-PEYRET, H. BÜRGER AND H. WILLNER

High resolution Fourier transform spectra of monoisotopic H_2^{80}Se have been recorded in the 2700-7000 cm^{-1} spectral domain and analysed leading to a precise set of experimental rotational levels for the (030), (110), (011), (120), (021), (200), (101), (002), (210), (111), (300), (201) and (102) vibrational states of this molecule. In order to fit these data to within their experimental uncertainty it proved necessary to consider explicitly the strong Coriolis and Darling-Dennison interactions between the $(\nu_1 \nu_2 \nu_3)$ and $(\nu_1 - 1 \nu_2 \nu_3 + 1)$, and $(\nu_1 \nu_2 \nu_3)$ and $(\nu_1 - 2 \nu_2 \nu_3 + 2)$ vibrational states respectively as well as weaker interactions. In this way, the experimental levels were calculated to within their experimental uncertainty and precise vibrational energies, and rotational and coupling constants were derived for all the studied states. These results together with those 1,2 concerning (000), (020), (100) and (001) were fit to obtain a set of equilibrium rotational constants and rotation-vibration interaction constants, and an improved equilibrium structure of the molecule has been obtained.

1. I.N. Kozin, S. Klee, P. Jensen, O. Polyansky and I. M. Pavkichenkov, *J. Mol. Spectrosc.* **158**, 409-422 (1993)

2. J.-M. Flaud, C. Camy-Peyret, H. Bürger and H. Willner, *J. Mol. Spectrosc.* **161**, 157-169 (1993)

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Address of H. Willner : Institut für Anorganische Chemie, Universität, 30167- Hannover, Germany

WE02 15 min 1:47

COMPARISON OF ABSORPTION SPECTRA IN THE RANGE 2000-1700 nm WITH POWER SPECTRA OF CLASSICAL TRAJECTORIES IN MOLECULES CONTAINING CH_2 GROUPS

GIOVANNA LONGHI and SERGIO ABBATE

It is generally thought that the vibrational spectra relative to the transition $\Delta v=2$ for XH_2 systems are intermediate between those typical of normal modes, which are observed for $\Delta v=1$, and those typical of local modes, which are observed for $\Delta v \geq 3$ (1), the parameters in the potential being the determining factor in higher or lower local mode character of the $\Delta v=2$ spectra. However the semiclassical method of the phase space spheres representing vibrational polyads introduced by Xiao and Kellman (2) poses some questions about this simple picture.

The absorption spectra at low resolution for molecules containing one or several equivalent CH_2 groups show two distinct types of behaviors at $\Delta v=2$, the first one with two band and the second with a characteristic couplet and a third band, with marked differences in intensities. The sum of power spectra of classical trajectories (3) for various total energies in a system of two coupled Morse oscillators, predicts in a quite qualitative way the existence of two bands at $\Delta v=1$, of three bands at $\Delta v=2$ and of one band at $\Delta v \geq 3$. However, in order to be more quantitative, it is found that semiclassical quantization conditions besides the right parameters in the model Hamiltonian are important in making the vibrational assignment.

1) I.M. Mills and A.G. Robiette, *Mol. Phys.*, **56**, 743 (1985)

2) L. Xiao, M.E. Kellman, *J. Chem. Phys.*, **90**, 6086 (1989)

3) D.W. Noid, M.L. Koszykowski, and R.A. Marcus, *J. Chem. Phys.* **67**, 404 (1977)

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WE03

10 min

2:04

THE POTENTIAL ENERGY FUNCTION OF CS₂ DERIVED FROM ROVIBRATIONAL DATA.

M. KOLBUSZEWSKI, P.R. BUNKER AND PER JENSEN

We have derived the potential energy surface of the $\tilde{X}^1\Sigma_g^+$ electronic state of CS₂ by adjusting it in a fitting to experimental rotation-vibration data. Using a variational approach and the Morse Oscillator Rigid Bender (MORBID) Hamiltonian, with a basis set composed of Morse oscillator stretching functions and rigid bender bending functions, we were able to fit twenty six vibrational band origins, up to 5000 cm⁻¹, and forty rotational level separations with $J < 6$; we obtain a root mean square deviation of 0.58 cm⁻¹ for the vibrational energies. The large masses of the terminal sulphur atoms lead to difficulties in basis set convergence because of large and unavoidable bend-stretch coupling in the kinetic energy operator. This effect has not been observed in previously studied hydrides such as CH₂, H₂O, H₂S, and H₂Te.

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WE04

15 min

2:16

A MODIFIED LENNARD-JONES OSCILLATOR MODEL FOR DIATOMIC POTENTIALS

Photos G. Hajigeorgiou and Robert J. Le Roy

Recent years have seen remarkable success in the development of flexible few-parameter model potentials able to accurately represent very large amounts of high quality data to spectroscopic accuracy, while simultaneously accounting for isotope and Born-Oppenheimer breakdown effects. However, even the best of these functions, the generalized Morse oscillator model,^{1,2} fails to take account of the theoretically known inverse-power long-range behaviour of internuclear potentials, and this limits the utility of such models for extrapolation or for determining dissociation energies. This paper addresses this question by proposing a new analytical representation for the internuclear potential energy of a diatomic molecule, which may be thought of as a generalization of the Lennard-Jones ($2n, n$) function,

$$U(R) = D_e \left[1 - \left(\frac{R_e}{R} \right)^n e^{-\beta(z)} \right]^2$$

where $\beta(z) = \beta_0 + \beta_1 z + \beta_2 z^2 + \dots + \beta_m z^m$, $z = 2(R - R_e)/(R + R_e)$ is the Ogilvie-Tipping expansion parameter, and n is the power of the leading term in the long-range inverse-power expansion for $U(R)$. As in any direct-fit method, the potential parameters can be determined in a nonlinear least-squares fit to spectroscopic line positions. The modified Lennard-Jones (MLJ) potential is compared with other functions for a variety of diatomic electronic states.

¹J.A. Coxon and P.G. Hajigeorgiou, *J. Mol. Spectrosc.* **150**, 1 (1991).

²H.G. Hedderich, M. Dulick, and P.F. Bernath, *J. Chem. Phys.* **99**, 8363 (1994).

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WE05

15 min

2:33

ANALYTICAL RADIAL HAMILTONIANS FOR THE $X^1\Sigma^+$ STATES OF HF AND HCl

John A. Coxon and Photos G. Hajigeorgiou

Over three years ago, we presented radial Hamiltonians for the $X^1\Sigma^+$ electronic states of hydrogen fluoride^{1,2} and hydrogen chloride³ which represented very accurately the wide range of spectroscopic data available on these important molecules. However, those functions were determined in numerical form on a radial grid, and despite their overall success in representing spectroscopic information, the Hamiltonians lacked compactness. In the present work, this problem is addressed by reducing the several thousand line measurements for HF, HCl, and related isotopomers, to Born-Oppenheimer potential functions which are modelled as modified Lennard-Jones (MLJ) oscillators⁴

$$U^{BO}(R) = D_e \left[1 - \left(\frac{R_e}{R} \right)^6 e^{-\beta(z)} \right]^2$$

where $\beta(z) = \beta_0 + \beta_1 z + \beta_2 z^2 + \dots + \beta_m z^m$, and $z = 2(R - R_e)/(R + R_e)$ is the Ogilvie-Tipping expansion parameter. The analysis also furnishes analytical functions which collectively describe adiabatic, homogeneous and heterogeneous non-adiabatic, relativistic, and quantum-electrodynamic effects.

In addition to the significant improvement in compactness, improved representations for the radial functions which describe the aforementioned effects have been developed, and fits using the new model yield direct estimates of the dissociation energies, D_e .

¹J.A. Coxon and P.G. Hajigeorgiou, *J. Mol. Spectrosc.* **142**, 254 (1990).

²W.T. Zemke, W.C. Stwalley, J.A. Coxon and P.G. Hajigeorgiou, *Chem. Phys. Lett.* **177**, 412 (1991).

³J.A. Coxon and P.G. Hajigeorgiou, *J. Mol. Spectrosc.* **139**, 84 (1990).

⁴P.G. Hajigeorgiou and R.J. Le Roy (see preceding abstract).

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WE06

15 min

2:50

METHODS AND SOME RESULTS OF STUDY FINE ROTATIONAL STRUCTURES
OF EXCITED VIBRATIONAL STATES OF POLYATOMIC MOLECULESO.N.Ulenikov

The methods which have been derived especially for analysing complicated vibration-rotation high resolution spectra of different type polyatomic molecules are discussed. The efficiencies of those methods are illustrated by the results of the first studies of some excited strongly interacting vibrational states of the CH_2D_2 , H_2Se , D_2S , HDS , and some other polyatomic molecules. Possibility of using of obtained information in the problem of determination of fundamental molecular parameters is discussed.

INTERMISSION

WE07 15 min 3:30

SpecSim - A GUI AND COMPUTATIONAL PROGRAM FOR THE MODELLING AND FITTING OF EXPERIMENTAL SPECTRA.

SERGEY I. PANOV AND TERRY A. MILLER

The SpecSim project was begun to develop a model independent GUI (Graphic User Interface) for spectral assignment. This MS Windows program evolved into a general purpose spectroscopic program that performs all the model independent calculations that are necessary for modelling and fitting molecular spectra. In addition to experimental spectra assignment SpecSim builds and diagonalizes different Hamiltonians, assigns quantum numbers to the calculated states, calculates intensities using model specific algorithms and creates simulated spectra with given Lorentzian and Gaussian lineshapes. The Levenberg-Marquardt NLLSQ fitting procedure is integrated into the program. SpecSim is written in the C++ computer language, and provides an easy mechanism for adding new models by attaching descriptive type software modules.

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WE08 15 min 3:47

EVALUATION OF ELECTRIC AND MAGNETIC PROPERTIES OF DIATOMIC MOLECULES FROM VIBRATION-ROTATIONAL SPECTRA OF SAMPLES WITHOUT EXTERNALLY APPLIED FIELDS
J. F. OGILVIE

We have developed a method based on well established equations that enables us to extract from the wavenumber data of vibration-rotational transitions of diatomic molecules in electronic states $^1\Sigma$ not only the molecular properties related to the definition of the radial functions for potential energy and related effects but also the electric dipolar moment and the rotational g factor. The latter quantity is related to the magnetisability and thus to the paramagnetic susceptibility independent of temperature, and this information is deduced from only the wavenumber data of multiple isotopic variants even though the spectra are measured, in absorption or emission, for samples without externally applied electric or magnetic fields. Accurate deductions of these electric and magnetic properties require highly accurate spectral measurements that may include both pure rotational transitions and vibration-rotational transitions, or just the latter. Applications of this method to spectra of diatomic molecules, particularly hydrides including AlH and GaH, will be critically discussed.

This research done partly in collaboration with S. C. Liao and E. Tiemann is supported financially by the National Science Council of the Republic of China

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WE09

15 min

4:04

DEFINITIVE EVALUATION OF NONADIABATIC VIBRATIONAL AND ADIABATIC EFFECTS
FROM VIBRATION-ROTATIONAL SPECTRA OF DIATOMIC MOLECULES
J. F. OGILVIE

Since van Vleck's original delineation of adiabatic, nonadiabatic rotational and nonadiabatic vibrational effects in the vibration-rotational spectra of diatomic molecules in 1936, there has been no definitive evaluation of these separate effects from experimental data. van Vleck undertook the analysis of the deviations of mass scaling of spectra by means of the analytic approach previously developed by Dunham in 1932 following earlier work by Born and Huckel in 1923. Based on much further development of the theory during the past seventy years, we have developed a method to evaluate the effects observable in the molecular transition wavenumbers related to specific terms in the effective hamiltonian related to these particular properties, and have applied this in a tested algorithm to real data from pure rotational and vibration-rotational spectra of selected molecules, neutral and ionic, in the electronic state $^1\Sigma^+$. In the absence of sufficient information from experimentally measured data, we have used computed results that simulate what is derived from experiment; the nature of these data indicate what further experimental measurements are valuable for diatomic molecules. The theory has been applied to LiH and to other species in electronic states $^1\Sigma^+$ that will be critically discussed.

This research done partly in collaboration with F. M. Fernandez, J. Oddershede, S. P. A. Sauer and J. T. Shy is supported financially by the National Science Council of the Republic of China

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WE10

15 min

4:21

THE USE OF TERM-VALUE FITS IN TESTING SPECTROSCOPIC ASSIGNMENTS

J. K. G. WATSON

The use of a least-squares term-value fit of a spectrum as a means of testing assignments is described. In a direct term-value fit the normal matrix is singular, with one zero eigenvalue for each set of connected levels. These equations are solved by a method which gives the term values of each connected set relative to their mean. The standard deviation σ from a term-value fit should be equal to the measurement error. It is shown that, as a test of individual assignments, it is possible to calculate from the results of a fit the fractional change $\tau_l = (\sigma_l - \sigma)/\sigma$ when each line l is omitted singly from the fit. Anomalously large negative values of τ_l indicate lines that may be misassigned or mismeasured. As an example, it is shown that the standard deviation of an unweighted term-value fit of a published compilation¹ of 294 lines of the H_3^+ ion can be reduced from 0.031 cm^{-1} to 0.004 cm^{-1} by the omission of 7 lines.

¹ L. Kao, T. Oka, S. Miller and J. Tennyson, *Astrophys. J. Suppl. Ser.* **77**, 317-329 (1991).

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WE11 15 min 4:38

CATASTROPHES IN ROTATIONAL ENERGY SURFACES OF MOLECULES WITH INTERNAL ROTATION JUAN ORTIGOSO AND JON T. HOUGEN

Rotational energy surfaces¹ (RES) are radial plots of the energy of a molecule as a function of the direction of the total angular momentum in the molecular fixed frame. RES are organized by the location and type of their stationary points, i.e., those points for which the gradient of the surface vanishes. Stationary points are important because classically, stable rotations can occur around axes from the origin to either maxima or minima on the RES.

The number of stationary points may change with the variation of some external parameter, as for example the total angular momentum J . Such changes are associated with stationary points for which the hessian vanishes. They are called catastrophe points and their distribution can explain qualitative changes in the energy level pattern of the molecule.

We have studied the catastrophe map for three torsional states of acetaldehyde below the barrier to internal rotation ($v_t=0,1,2$) and the first state above the barrier ($v_t=3$), for both A and E torsional symmetry species, and for values of $J < 35$. The number of stationary points for $v_t=0,1,2$ A states is six for all J values examined, a result identical to that obtained for any rigid asymmetric rotor. For $v_t=0,1$ E states, where torsion-rotation interactions are larger, the number is still six. However, the E states for $v_t=2$ present a number of catastrophes as J increases which create or annihilate pairs of stationary points. For $v_t=3$ E states the situation is even more complicated, so that for $J=25$ there are 20 stationary points. The catastrophe history (with J) of these RES can be followed, beginning with the stationary points (2 maxima, 1 saddle, 1 minimum) which exist for $J=1$. The relevance of these catastrophes for the energy levels of acetaldehyde will be discussed in terms of the changes in the trajectories of the angular momentum vector as a consequence of the changes in the topology of RES.

¹W. G. Harter and C. W. Patterson, J. Chem. Phys. **80**, 4241 (1984).

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WE12 15 min 4:55

ELECTRIC-FIELD INTERACTIONS IN VIBRATIONALLY HIGHLY EXCITED MOLECULES: THE $5\nu_1$ BAND OF HCCF JUAN ORTIGOSO, GERALD T. FRASER AND BROOKS H. PATE

Recent experiments have shown that the mechanism of the Stark shift for molecules in regions of high state density is complicated at the eigenstate level. Essentially, the eigenvalue positions do not show much movement with changing electric-field strength, however, the eigenvector components (and therefore the intensities) vary dramatically with strength. In an attempt to understand this kind of phenomenon we are modelling the influence of an electric field on the infrared spectrum of HCCF in the region corresponding to five quanta of the CH stretch. Our model considers explicitly four kinds of Fermi resonances plus the off-diagonal ℓ -resonance interaction as proposed by Vaittinen et al.¹ The effect of these resonances is to break the Hamiltonian matrix into a series of Fermi polyads. Although the dimension of these submatrices is still large (several thousands) it is possible to reduce their size in a drastic way by using a tier model which only takes into account sequential couplings between the zeroth order states. The electric field destroys the J quantum number, complicating the problem, but it is still possible to reduce the size of the matrices by including the operator $\mu E \cos \theta$ in the tier scheme.

¹O. Vaittinen, M. Saarinen, L. Halonen and I. M. Mills, J. Chem. Phys. **99**, 3277 (1993).

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Address of Pate: Department of Chemistry, University of Virginia, Charlottesville, VA 22901.

WE13

15 min

5:12

VIBRATIONAL ENERGY RELAXATION BEYOND THE GOLDEN RULE: NEW
HIGH-RESOLUTION AND ULTRAFAST PERSPECTIVES,
R.M. BIGWOOD AND M. GRUEBELE

A scaling law for anharmonic vibrational couplings is used to estimate the vibrational redistribution (IVR) rates and line shapes for excited polyatomic molecules.¹ Among the interesting results of this analysis are a breakdown of the Golden Rule even in cases where line shapes appear Lorentzian: rates appear to increase *linearly* with the coupling strength. The model includes as special cases several 'tiered' approximations to IVR, and promises interesting possibilities of molecular control with ultrafast or energy resolved lasers via quantum coherence effects.

R.M. Bigwood and M. Gruebele, Chem. Phys. Lett., submitted for publication.

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WE14

10 min

5:29

The potential energy surface for the electronic ground state of H_2^{16}O determined with a new level of accuracy

Oleg L. Polyansky, Per Jensen, and Jonathan Tennyson

The potential energy function for the electronic ground state of the water molecule has been obtained by fitting rotation-vibration term values involving $J \leq 14$ for 24 vibrational states of H_2^{16}O together with 25 additional vibrational term values belonging to higher excited states. The fitting was carried out by means of an exact kinetic energy Hamiltonian. It was found that the differences between the exact kinetic energy calculations and calculations with the MORBID program (i.e., calculations with an approximate kinetic energy operator) depend only very slightly on the particular parameters of the potential. This fact allowed us to make an inexpensive fitting using the MORBID approach and still get the accuracy obtainable with the exact kinetic energy Hamiltonian. The standard deviation for 1600 term values was 0.36 cm^{-1} . For 220 ground state energy levels the standard deviation was 0.03 cm^{-1} . With the fitted potential, calculations of term values with $J \leq 35$ were carried out. This showed the excellent predictive power of this potential. For instance the discrepancy for the highest observed $K_a = 20$ level of the ground state, 20_{200} , is only 0.001 cm^{-1} . The discrepancy for the observed level with the highest J , 35_{035} was 0.1 cm^{-1} . Because of the level of accuracy achieved in these calculations, we can for the first time demonstrate the breakdown of the Born-Oppenheimer approximation for the water molecule. The high K_a level calculations allow us to show that the rotational energy level structure in water is at least of a very different nature than the four-fold cluster structures observed for H_2Se and calculated for H_2S , H_2Se and H_2Te .

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WF01 10 min 1:30

LOW TEMPERATURE HELIUM PRESSURE BROADENING OF OCS, 4 - 20K,
K. A. ROSS, K. RAMADAS, W. A. NEFF AND D. R. WILLEY

The pressure broadening cross sections of OCS broadened by helium were measured for the $J = 1 - 2$, $J = 2 - 3$ and $J = 3 - 4$ rotational transitions of OCS. The experiment was performed in a collisionally-cooled cell at temperatures ranging from 4 - 20 K. At 20 K cross sections for all three transitions are 40-50% larger than their 300 K counterparts. From 20 to 4 K cross sections show a slight decrease with temperature and at 4 K are 10-20% larger than the 300 K values. The low temperature data will be compared to cross sections calculated from existing OCS-He potential surfaces and attempts at producing an improved OCS-He potential will be presented.

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WF02 15 min 1:42

THE VARIABLE TEMPERATURE PRESSURE BROADENING SPECTRUM OF CO ON HYDROGEN

D. C. FLATIN, T. M. GOYETTE, AND F. C. DE LUCIA

A system has been developed which has allowed us to measure the hydrogen pressure broadening parameters of CO, H₂S, and CH₃F between approximately 5K and 100K. In combination with other experimental systems, this has allowed measurements over a 5K to 1000K range. In the semiclassical region above ~100K, the behavior of the cross sections for collisions with hydrogen is more complex than comparable collisions with helium because of the additional rotational degrees of freedom in the hydrogen molecule. At low temperatures very significant increases in cross section, which are associated with the quasibound states, are observed. New results for CO hydrogen broadening will be discussed. Some comparisons will be made with measurements of other molecular systems. The apparatus will be described as will experimental results and their relationship to theoretical predictions.

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WF03 15 min 1:59

THE MICROWAVE SPECTRUM AND STRUCTURE OF THE PYRIDINE··CO COMPLEX

R. P. A. BETTENS AND A. BAUDER

The microwave spectra have been measured and assigned for 5 isotopic species of the pyridine··CO complex. The spectra contained no evidence for large amplitude motions, *i.e.*, no perturbations nor splittings other than hyperfine were observed. The size of the centrifugal distortion constants also implied a relatively strongly bound complex. CO was expected to lie above the aromatic ring plane as was found for the diatomic monomer in benzene··CO, pyrrole··CO and benzene··N₂. However, in pyridine··CO the CO is located in the ring plane of pyridine, the complex being planar ($\Delta_0 \approx -0.76 \text{ u}\text{\AA}^2$). r_0 and r_s structures have been determined each yielding two possible structures for the complex, although one structure agrees better with the spectroscopic data than the other. Again we were surprised to discover that CO did not lay along the C_2 axis of pyridine. This was clearly indicated by the presence of two dipolar types of transitions in the spectra and from the structural analysis. The structure of the complex will be presented and a comparison with the benzene··CO, pyrrole··CO and furan··HCl complexes will be made.

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WF04 15 min 2:16
MICROWAVE SPECTRUM AND STRUCTURE OF HF-BF₃

E.J. Campbell, J.A. Phillips, H. Goodfriend, A. Grushow, M. Canagaratna, J. Almlöf, and K.R. Leopold

A new pulsed-nozzle Fourier transform microwave spectrometer has been used to study the complex HF-BF₃. A symmetric top spectrum is observed with $B=3327.3361(24)$ MHz, $D_J=0.01097(36)$ MHz, $D_{JK}=0.0504(10)$ MHz, and $eqQ_{aa}=2.7833(53)$ MHz for the ¹¹B species, and $B=3334.9078(12)$ MHz, $D_J=0.01117(12)$ MHz, $D_{JK}=0.05183(39)$, and $eqQ_{aa}=5.765(11)$ for the ¹⁰B species. The data are consistent with a fluorine-bonded structure with an unexpectedly short intermolecular B-F bond length of 2.51 Å. *Ab initio* calculations, which greatly facilitated location of the spectrum, further predict an approximately 2° out-of-plane distortion of the BF₃ in the complex, and a B-F-H bond angle of 108°. This latter result suggests that the complex is a symmetric top due only to rapid vibrational averaging of the HF orientation. The short bond length and the small but non-zero distortion of the BF₃ are indicative of an incipient donor-acceptor interaction, which is somewhat surprising for fluorine.

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WF05 15 min 2:33
THE MICROWAVE SPECTRUM AND STRUCTURE OF THE METHYLACETYLENE•SO₂ COMPLEX

Xue-Qing Tan, Li-Wei Xu, and Robert L. Kuczkowski

The microwave spectrum of the methylacetylene•SO₂ (MA•SO₂) complex has been observed using a pulsed nozzle, molecular beam Fourier transform microwave spectrometer. Two different large amplitude internal motions were observed. The methyl group internal rotation splits each rotational transition of the complex into A and E components; an SO₂ inversion motion further splits each A and E level into doublets. The structure of the complex was determined using the rotational constants of the normal species as well as MA•S¹⁸O¹⁶O, and the dipole moment data. The SO₂ was found to sit above the carbon-carbon triple bond, with its symmetry axis twisted away from parallel to the symmetry axis of the methylacetylene by about 60°. We are proceeding with the assignment of the E transitions and will report a global fit of all the rotational transitions.

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WF06 15 min 2:50
TUNNELING MOTIONS AND METASTABLE ISOTOPOMERS IN THE MICROWAVE AND SUBMILLIMETER SPECTRA OF MIXED DEUTERATED-PROTONATED WATER DIMERS

E.N. Karyakin, G.T. Fraser, R.D. Suenram, F.J. Lovas, A. Grushow, M.A. Burns, K.R. Leopold, and M. Fujitake

An electric-resonance optothermal spectrometer with frequency synthesizers and phase-locked backward-wave oscillators, a slit-jet molecular-beam with a CO₂-laser difference-frequency microwave-sideband spectrometer, and a pulsed-nozzle Fourier-transform microwave spectrometer are used to investigate the nine mixed deuterated-protonated isotopomers of water dimer. The use of He and mixed He-Ne carrier gases allows the observation of the metastable O--H bonded isotopomers, not observed in previous studies in Ar beams. Spectra are observed for the $K = 0 \leftarrow 0$, $K = 1 \leftarrow 1$, and $K = 1 \leftarrow 0$ subbands. The spectra are complicated by the tunneling interchange of equivalent proton or deuterons and, for the two (HOD)₂ isotopomers, by the tunneling interchange of the hydrogen-bond donor and acceptor roles of the two HOD moieties. To guide the assignments microwave or submillimeter - radiofrequency double resonance is used, together with the observation that the A, B, and C rotational constants and methyl-amine type tunneling splittings are nearly insensitive to isotopic substitution of the deuteron/proton in the hydrogen bond. The tunneling splittings and tunneling state selection rules furnish a critical test of proposed tunneling pathways in the water dimer.

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Address of Fraser, Suenram, and Lovas: Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, MD 20899.

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INTERMISSION

WF07 15 min 3:30
THE ν_{K_A} BRANCHES ($K_A \in \{2, 3, 4\}$) OF CARBODIIMIDE, HNCNH

V. WAGENER, M. BELLINI, and M. WINNEWISSE

The ν_{K_A} branches ($K_A \in \{2, 3, 4\}$) of carbodiimide, HNCNH, have been recorded with the tunable far infrared spectrometer available at the European Laboratory for Nonlinear Spectroscopy (LENS)^a.

The main purpose of our measuring campaign at LENS was to record the rotationally resolved spectrum of the low-lying (≈ 2.4 THz) bending vibration ν_7 of tricarbon oxide sulfide, OC₃S. This work was presented at the Thirteenth Colloquium on High Resolution Molecular Spectroscopy at Riccione^b. We used the strong Q -branch transitions of HNCNH to tune the spectrometer in order to observe the very weak transitions of the ν_7 -band system of OC₃S. The spectra obtained by this procedure contain new information on HNCNH.

HNCNH, which exists in equilibrium with cyanamide in the vapour phase, is a skew-chain molecule and by accident a nearly perfect symmetric top with $\kappa = -0.999\,995\,368(18)^c$. The ν_{K_A} branches which occur at approximately 1.8 THz, 2.5 THz and 3.2 THz, respectively, could be recorded rotationally resolved. A torsional doublet splitting was observed in all Q -branches. In addition asymmetry splitting could be detected within the ν_{Q_2} branch for $J > 18$.

The spectra and the analysis will be presented.

^aL.R. Zink, P.De Natale, F.S. Pavone, M. Prevedelli, K.M. Evenson, and M. Inguscio *J. Mol. Spectrosc.* **143**, 304-310 (1990).

^bV. Wagener, and M. Winnewisser *Thirteenth Colloquium on High Resolution Molecular Spectroscopy K 27*, Riccione (1993).

^cM. Birk, M. Winnewisser, and E.A. Cohen *J. Mol. Spectrosc.* **136**, 402-445 (1989).

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WF08 15 min 3:47

ROTATIONAL SPECTRA, ^{27}Al AND ^{14}N NUCLEAR QUADRUPOLE COUPLING
CONSTANTS AND MOLECULAR STRUCTURE OF TRIMETHYLAMINE ALANE
(CH_3) $_3\text{NALH}_3$, H. E. WARNER, Y. WANG, C. WARD AND C. W. GILLIES

The high resolution rotational spectra of (CH_3) $_3^{14}\text{NALH}_3$, (CH_3) $_3^{15}\text{NALH}_3$, (CH_3) $_3^{14}\text{NALD}_3$, (CH_3) $_3^{14}\text{NALHD}_2$ and (CH_3) $_3^{14}\text{NALH}_2\text{D}$ are reported using a recently constructed pulsed-nozzle Fourier-transform microwave spectrometer. The ^{27}Al and ^{14}N hyperfine structure in (CH_3) $_3^{14}\text{NALH}_3$ and (CH_3) $_3^{14}\text{NALD}_3$ have been fit to a standard Hamiltonian for two quadrupolar nuclei. The analysis for (CH_3) $_3^{14}\text{NALH}_3$ gives $B = 2745.113(1)$ MHz, $D_J = 643(4)$ Hz, $D_{JK} = 1372(250)$ Hz, $eQq(^{27}\text{Al}) = 25.032(6)$ MHz and $eQq(^{14}\text{N}) = -3.777(5)$ MHz. A combination of all the microwave isotopic moments of inertia with an electron diffraction study determines the complete molecular structure. This work provides the first measurement of a gas phase ^{27}Al nuclear quadrupole coupling constant in a polyatomic aluminum compound. The aluminum-nitrogen bond distance and $eQq(^{27}\text{Al})$ are related to the dissociation energy of the dative bond in (CH_3) $_3\text{NALH}_3$. Comparisons are also made with analogous boron-nitrogen donor-acceptor complexes.

1. A. Almenningen, G. Gundersen, T. Haugen and A. Haaland, *Acta Chem. Scand.* **26**, 3928 (1972).

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WF09 15 min 4:04

MICROWAVE SPECTRUM OF $\text{CF}_3\text{CH}_2\text{OH}$, C. W. GILLIES, H. E. WARNER, J. Z. GILLIES, G. FRASER, F. J. LOVAS, AND R. D. SUENRAM

A study of the low resolution rotational spectrum of $\text{CF}_3\text{CH}_2\text{OH}$ employing a Stark-modulated absorption spectrometer as well as an optoacoustic microwave spectrometer identified two series of bands which fit the relation $\nu \approx (2A-B-C)(K_1 + 1/2)$.¹ These bands were assigned to b -type Q-branch series characteristic of a nearly-prolate rotor. Utilizing the high resolution of a pulsed-beam Fourier-transform spectrometer, μ_a - and μ_b -type transitions have been assigned for two states in $\text{CF}_3\text{CH}_2\text{OH}$. The transitions cannot be satisfactorily fit to an asymmetrical top Watson Hamiltonian presumably because the two states involved are Coriolis coupled. However, a large number of combination differences confirm the low J energy level structure for each state. Currently, optothermal microwave studies are underway to obtain high frequency data in order to understand the origin of the spectral perturbations.

1. S. P. Sponseller and C. W. Gillies, 35th Symposium on Molecular Spectroscopy, Paper RC5, 1980, Ohio State University, Columbus, Ohio.

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WF10 10 min 4:21

THE SUBMILLIMETER-WAVE SPECTRUM OF PROPIONITRILE (C_2H_5CN)

J. C. PEARSON, K. V. L. N. SASTRY, ERIC HERBST, AND FRANK C. DE LUCIA

The ground state rotational spectrum of propionitrile was observed in the 259 - 610 GHz frequency range. A total of 952 transitions including 732 newly measured ones through $J = 70$ and $K_a = 36$ were fit to a Watson A-reduced Hamiltonian with a root-mean-square deviation of 61 kHz. The fit determined the rotational constants A, B and C along with a complete set of quartic and sextic distortion constants and six octic distortion constants. No splittings due to internal rotation or the ^{14}N quadrupole were observed. The refinement of the constants should have improved predictive power over the previous analysis¹, especially at high J values.

¹F. J. Lovas, *J. Phys. Chem. Ref. Data*, **11**, 251 (1982).

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WF11 15 min 4:33

THE MILLIMETER-WAVE AND SUBMILLIMETER-WAVE SPECTRUM OF PROPYLENE (CH_3CHCH_2)

J. C. PEARSON, K. V. L. N. SASTRY, ERIC HERBST AND FRANK C. DE LUCIA

The ground state rotational-torsional spectrum of the internal rotor propylene (CH_3CHCH_2) was observed in the millimeter-wave and the submillimeter-wave regions with a klystron based spectrometer. Approximately 760 lines in the A and E substates of the ground torsional state were measured. Rotational transitions with quantum numbers through $J = 30$ and $K_a = 22$ were observed up to a frequency of 412 GHz. The newly measured lines were combined with the approximately 40 transitions measured by Hirota¹ and Lide and Mann² and fit to 90 kHz with an internal axis Hamiltonian. The spectroscopic constants A, B, C, five quartic and three sextic distortion constants, and the three internal rotation parameters D_{ab} , V_3 and ρ were determined. These constants along with the previously determined values of V_6 and F should permit accurate prediction of many unmeasured rotational transitions.

¹E. Hirota, *J. Chem. Phys.* **45**, 1984-1990 (1966).

²D. R. Lide, JR. and D. E. Mann, *J. Chem. Phys.* **27**, 868-873 (1957).

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WF12 15 min 4:50
THE MILLIMETER-WAVE SPECTRUM OF METHYL FORMATE (HCOOCH_3) AND SYMMETRIC DEUTERATED METHYL FORMATE (DCOOCH_3)

L. C. OESTERLING, D.W. FERGUSON, E. HERBST, AND F.C. DE LUCIA

Although deuterated isotopomers of organic molecules have been detected in various interstellar sources, singly deuterated isotopomers have not yet been detected in the interstellar medium due to a lack of spectroscopic data. To aid in the analysis of interstellar spectra, rotational transitions in the ground ($v_t=0$) A (symmetric) and E (asymmetric, degenerate) torsional states of deuterated and normal methyl formate were measured on a TWT based broadband spectrometer. In order to minimize the rotation-torsion coupling, the data were analyzed via a diagonalization procedure involving an extended internal-axis method (IAM) Hamiltonian for angular momentum quantum number $J \leq 35$.

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WF13 10 min 5:07

PRECISION BROADBAND SPECTROSCOPY IN THE TERAHERTZ REGION, S. P. BELOV, M. LIEDTKE, G. WINNEWISSER, K.M.T. YAMADA, J. BEHREND, TH. KLAUS, R. SCHIEDER, A.H. SALECK, M.YU. TRETYAKOV, AND A.F. KRUPNOV

For the first time precision broadband spectroscopic measurements have been performed in the spectral region up to 1.1 THz. Continuous frequency coverage and microwave accuracy are achieved by employing frequency and phase stabilized Backward Wave Oscillators (BWOs). This breakthrough in high-resolution scanning spectroscopy became possible by the opening of the borders between East and West and essentially by the collaborative efforts between Cologne University, Germany, and the Institute of Applied Physics, Nizhnii Novgorod, Russia.^a Extensive measurements have been performed on HSSH, HOOH, their various isotopomers, and astrophysically relevant molecules and radicals. Some of their spectra will be presented.

We have performed extensive measurements of the $^1\text{QK}_a$ branches for $K_a \geq 2$ of HSSH and its various isotopomers for two purposes: (i) to obtain new spectroscopic information concerning the anomalous K-doubling and the mass dependence of the torsional problem and (ii) to demonstrate the hitherto unknown wide tunability of the employed BWO's and the high sensitivity of the new Cologne terahertz spectrometer.

The essential components of the Cologne spectrometer system^b consist of the BWO's supplied by the ISTOK Research and Production Company (Fryazino, Moscow region), a newly designed multiplier-mixer with low noise HEMT amplifier, two millimeter-wave synthesizers (78 to 118 GHz; 118-178 GHz, from the Institute of Electronic Measurement, KVARZ, Nizhnii Novgorod), and a He-cooled InSb detector.

^a M. Liedtke et al., J. Mol. Spectrosc. 161, 317-321 (1993).

^b G. Winnewisser et al., J. Mol. Spectrosc. 165, 294-300 (1994).

Address of J. Behrend, S.P. Belov, Th.Klaus, M. Liedtke, A.H. Saleck, R. Schieder, G. Winnewisser and K.M.T. Yamada: I. Physikalisches Institut, Universitaet zu Koeln, D-50937 Koeln, Germany

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WF14**15 min****5:19****THE VARIABLE TEMPERATURE PRESSURE BROADENING SPECTRUM OF CH_3F ON HELIUM****M. M. BEAKY, T. M. GOYETTE, AND F. C. DE LUCIA**

A system has been developed which has allowed us to measure the helium pressure broadening parameters of H_2S and CH_3F between approximately 1K and 100K. In combination with other experimental systems, this has allowed measurements over a 1K to 1000K range. This range is wide enough to clearly observe the transition from the high temperature semiclassical regime in which the physics of the collision is properly described by Anderson-like theories to a low temperature regime in which new phenomena associated with quasibound states require a more complete quantum mechanical description. New results for CH_3F helium broadening will be discussed. Some comparisons will be made with measurements of previous experiments and with other molecular systems. The apparatus will be described as will experimental results and their relationship to theoretical predictions.

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WG01 30 min 1:30

CORE-NONPENETRATING RYDBERG STATES: SPECTROSCOPIC BLACK HOLES, R.W. FIELD, Z. JAKUBEK, N. HARRIS, AND C. GITTINS.

At first glance the exchange of energy and angular momentum between a particle as light as an electron and a system as heavy as a molecular cation seems improbable and inefficient. Molecular Rydberg spectra can reveal the nature and strengths of the e^- /ion coupling mechanisms. Our studies of the alkaline earth monohalides (CaF, CaCl, BaF), examples of a uniquely simple e^- /MX⁺ system consisting of two closed shell atomic ions (M²⁺ and X⁻) where MX⁺ has enormous and easily calculable multipole moments, have revealed the outline of a simple picture of the e^- /MX⁺ interaction mechanisms. There are two types of Rydberg series, **core-nonpenetrating** (near-integer effective principal quantum number n^* , negligible ℓ -mixing, rapid ℓ -uncoupling, unusual sensitivity to isotopic substitution or vibrational excitation through dependence of the multipole moments on the M²⁺ to center-of-mass distance) and **core-penetrating** (severe ℓ -mixing among *all* of the *penetrating*- ℓ -values as manifest in s~p~d or s~p~d~f supercomplexes, slow and incomplete ℓ -uncoupling, and n^* -scaling of fine structure parameters¹). The structure and dynamics of nonpenetrating series are well described by a long-range multipole model^{2,3}. Each penetrating series may be viewed as built on an $n^{*-3/2}$ -scaled replica of a valence state¹, where the valence state is well described by ligand field theory⁴. The picture is completed by outside-the-core dipole and quadrupole interactions between penetrating and nonpenetrating series⁵. Although, by revealing the values of the ion-core multipole moments and polarizabilities, the nonpenetrating series should play a central role in describing the e^- /ion interaction, these series have been surprisingly resistant to direct, systematic exploration.

¹ J.M. Berg, J.E. Murphy, N.A. Harris, and R.W. Field, Phys. Rev. A **48**, 3012 (1993).

² Ch. Jungen and E. Miescher, Canad. J. Phys. **47**, 1770 (1969).

³ E.E. Eyler and F.M. Pipkin, Phys. Rev. A. **27**, 2462 (1983).

⁴ S.F. Rice, H. Martin, and R.W. Field, J. Chem. Phys. **82**, 5023 (1985).

⁵ Z.J. Jakubek and R.W. Field, Phys. Rev. Lett. (1994).

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WG02 15 min 2:05

THE NON-PENETRATING RYDBERG STATES OF CaF, N. HARRIS, C. GITTINS AND R.W. FIELD.

Nearly every member of all six core-penetrating Rydberg series ($\ell < 3$) of CaF has been observed (from the ground state through $n^* = 10$) and is fairly well characterized¹. The non-penetrating states ($\ell > 2$), however, had stubbornly evaded detection. These non-penetrating states are easy to identify because they have near integer n^* and some have anomalous rotational constants (the upper component of the complex can have an effective rotational constant about 20% larger than that of the ion) at relatively low n^* due to rapid ℓ -uncoupling. Non-penetrating states, which are seldom observed in molecular Rydberg spectra, provide important information about the multipole moments and polarizabilities of the CaF⁺ ion that is difficult to derive from the core-penetrating series but essential for an understanding of the exchange of energy and angular momentum between the Rydberg e^- and the molecular ion core. For example, it has been shown that the splittings between the different λ -components of an f complex are a measure of the quadrupole moment^{2,3}.

Most CaF Rydberg spectra were recorded in OODR fluorescence based experiments using selected rotation-vibration levels of the A²Π state as the intermediate state^{1,4}. Those experiments discriminate doubly (both excitation and detection) against the observation of high- ℓ states. New spectra of the Rydberg states of CaF have been recorded. These include REMPI-TOF and fluorescence-based experiments. The new fluorescence-based experiments use the C²Π state as the intermediate state. The C²Π state is a member of a different Rydberg series than the A²Π state, so it has both different dominant " ℓ " character as well as more amplitude outside the core. Thus the C²Π state will have better overlap with the non-penetrating series. Using the C²Π state as the intermediate state, we have observed and assigned states with anomalously large and small effective rotational constants. The REMPI-TOF experiments complement and extend the fluorescence data into the autoionizing $v = 1, n^* > 12.7$ region.

¹ J.M. Berg, J.E. Murphy, N.A. Harris, and R.W. Field, Phys. Rev. A **48**, 3012 (1993).

² Ch. Jungen and E. Miescher, Canad. J. Phys. **47**, 1770 (1969).

³ E.E. Eyler and F.M. Pipkin, Phys. Rev. A. **27**, 2462 (1983).

⁴ J.E. Murphy, Ph.D. Thesis, MIT (1992).

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WG03

15 min

2:22

AUTOIONIZING RYDBERG STATES OF CaCl, C. GITTINS, N. HARRIS, AND R. W. FIELD

Rotationally resolved, vibrational autoionization detected, optical-UV double resonance spectra of CaCl have been observed above the $v=0$ ionization threshold. The observed Rydberg states have $n^*>15$ and $v=1$. The experiment is a variation on traditional optical-optical double resonance (OODR) experiments in that the signal is produced by autoionization, rather than by UV fluorescence or a fluorescence dip. All spectra were recorded using $A^2\Pi_{3/2}-X^2\Sigma^+_{1/2}(0,0)$ PUMP transitions^{1,2}. The Rydberg- $A^2\Pi_{3/2}(1,0)$ transitions are in the near UV. Vibrational autoionization is found to be much more efficient than direct ionization from $A^2\Pi_{3/2}, v=0$ to $(CaCl)^+, v^+=0$.

As the most useful $Ca^{35}Cl$ and $Ca^{37}Cl$ PUMP transitions are often coincident, double resonance does not always discriminate between the two isotopic species. The isotopomers are distinguished by detecting $(CaCl)^+$ in a time-of-flight mass spectrometer. The isotope effect also provides absolute vibrational assignment of Rydberg- $A^2\Pi_{3/2}$ transitions. Several series have been followed from $n^*=15$ through 43. The $n^*=16$ supercomplex has been analyzed in detail. The observed spectra cannot be explained in terms of pure- ℓ states^{3,4}. An abrupt decrease in the density of observed transitions occurs near $n^*=25$. This effect is believed to be a result of the opening of a predissociation channel. The CaCl ionization potential has been (spectroscopically) determined to be 6.012(1) eV. The $(CaCl)^+$ rotational constant and vibrational frequency will also be reported.

1. L.-E. Berg, L. Klynning, and H. Martin, *Phys. Scr.* **21**, 173-178 (1980).
2. W. E. Ernst, J. O. Schröder, U. Buck, J. Kesper, and T. Seelemann, *J. Mol. Spectrosc.* **117**, 342-354 (1986).
3. J. E. Murphy, J. M. Berg, A. J. Merer, N. A. Harris, R. W. Field, *Phys. Rev. Lett.* **65**, 1861-1864 (1991).
4. N. A. Harris and C. Jungen, *Phys. Rev. Lett.* **70**, 2549-2552 (1993).

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WG04

15 min

2:39

BAF $v=1$ RYDBERG STATES: AUTOIONIZATION, SUPERCOMPLEXES, AND BLACK HOLES
ZYGMUNT J. JAKUBEK AND MA HUI.

Barium monofluoride $v=1$ Rydberg states in the range of $13.6 \leq n^* \leq 56$ have been observed in a mass resolved ionization detected OODR experiment. The BaF molecules were produced in a high temperature effusive beam source. Below $n^*=36$ spectra were recorded via $6.5 \leq J \leq 11.5$ f-symmetry intermediate levels in the $C^2\Pi_{3/2} v=0$ state. Above $n^*=36$ only one set of spectra with $J=6.5f$ in the intermediate state was obtained. Below the $v=0$ ionization threshold ($n^*=14.3$) BaF^+ ions detected in TOF were produced via field ionization: $E = 400$ V/cm. Above the $v=0$ ionization potential vibrational **autoionization** is believed to be the dominant BaF^+ ion-producing mechanism. Only a small line broadening was observed; at $n^*=15$ autoionization widths were estimated to be <0.02 cm⁻¹. In the region of $13.6 \leq n^* \leq 22$ the spectra reveal characteristic structure of *s-p-d-f* **supercomplexes** known from our previous experiments on BaF $v=0$ states¹. Most of the lines are grouped slightly below and above integer n^* with a virtually line-free region at integer n^* . This line-lacking region, surrounded by clusters of lines below and above we call a **spectral black hole**. For $n^*>22$ the black hole structures are no longer so readily evident, but separate *s-p-d-f* supercomplexes can be still identified up to $n^*=30$. A detailed analysis of the $n^* = 14 - 22$ *s-p-d-f* supercomplexes will be presented.

¹ Z. J. Jakubek and R. W. Field, *Phys. Rev. Lett.* (1994)

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WG05 15 min 2:56

**PULSED FIELD IONIZATION ZERO KINETIC ENERGY ELECTRON
SPECTROSCOPY OF A PREDISSOCIATING STATE OF HBr^+ ($\text{A}^2\Sigma^+$)**

J.D.D. Martin, A. Mank, T. Nguyen, and J.W. Hepburn

With a tunable coherent extreme ultraviolet light source, we have studied the threshold photoionization of HBr ($\text{X}^1\Sigma^+$, $v=0$) to HBr^+ ($\text{A}^2\Sigma^+$, $v^+=0,1,2,3$) using pulsed field zero kinetic energy electron spectroscopy (PFI-ZEKE). The rotationally resolved data provide new spectroscopic information on the $v^+ > 1$ final states, which are known to predissociate into H and Br^+ fragments. Line broadening has been observed for $v^+=3$.

Spin-rotation splitting is observed for $v^+=0,1,2$. The rotational linestrengths have been modelled using the direct photoionization model of Buckingham, Orr and Sichel.¹

1) A.D. Buckingham, B.J. Orr, and J.M. Sichel, Philos. Trans. R. Soc. London Ser A **268**, 147 (1970).

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INTERMISSION

WG06 30 min 3:30

MEASUREMENTS OF EXCITED STATES IN MOLECULAR HYDROGEN TO 1 PART IN 10^8 , E.E. EYLER

At this conference four years ago, a measurement of the ionization potential of H_2 accurate to 0.015 cm^{-1} was described. This talk will emphasize the rapid progress that has been made since then. The majority of recent experiments employ a two-step approach, in which highly excited levels are measured relative to the EF ($2s\sigma$) $^1\Sigma_g^+$ state. The EF state energy levels are measured in a separate experiment.

My research group has very recently succeeded in measuring two-photon $EF \leftarrow X$ intervals in H_2 , HD, and D_2 to an accuracy of 0.001 cm^{-1} , or 1 part in 10^8 . A pulse-amplified single-mode cw laser is used in a Doppler-free counterpropagating-beam configuration. The main difficulty is that substantial optical phase distortion occurs during pulsed amplification of a laser. To overcome this, we measure the optical phase directly using a heterodyne scheme. These measurements are thought to be the most accurate spectroscopic results ever obtained using pulsed lasers.

From the EF state, higher Rydberg states can be accessed. This allows both the investigation of excited-state structure and dynamics, and experimental determinations of the ionization potential and dissociation energy. During the past few years experiments of this type have been conducted both by Herzberg and coworkers¹ and by my own research group.² In this talk I will describe one example of this work, a measurement of the ionization potential of HD by extrapolation of the high Rydberg np states.¹ Agreement of theory with experiment is presently quite good, though there are hints of a possible small mass-dependent discrepancy. The hydrogen molecule thus continues to serve as one of the key benchmarks for testing molecular physics, including tests of quantum electrodynamics at the 5% level and beyond.

¹Ch. Jungen, I. Dabrowski, G. Herzberg, and M. Vervloet, J. Chem. Phys. **93**, 2289 (1990); also J. Mol. Spectrosc. **153**, 11 (1992).

²J.M. Gilligan and E.E. Eyler, Phys. Rev. A **46**, 3676 (1992); E.E. Eyler and N. Melikechi, Phys. Rev. A **48**, R18 (1993).

WG07 15 min 4:05

LASERSPECTROSCOPIC INVESTIGATION OF HIGHER EXCITED ELECTRONIC STATES OF KAr
R. Michalak, D Zimmermann

First successful measurements on higher excited electronic states of the van der Waals molecule KAr have been performed in a supersonic jet. The higher excited electronic states 2Λ are reached in a two-step excitation via the intermediate state $A^2\Pi$ using two tunable cw dye lasers. One laser, the pump laser with $\lambda \approx 770$ nm, was tuned to a suitable rovibrational line of the $A^2\Pi \leftarrow X^2\Sigma$ transition populating one rovibrational sublevel of the $A^2\Pi$ state. The second probe laser ($\lambda \approx 585$ nm) was scanned over a range of about 200 cm^{-1} . By means of a systematic variation of the pumping transition we found a total of more than 500 lines due to the transition $2\Lambda \leftarrow A^2\Pi$.

A large part of these lines could be assigned to the rotational structure of vibrational bands leading to vibrational levels of the two 2Σ states being correlated with the 7^2S and the 5^2D state of the K-atom. In addition, the parameters of rotation and of spin-orbit coupling could be determined for 6 and 3 vibrational levels due to the $2\Delta(5^2D)$ and the $2\Pi(5^2D)$ state, respectively. For the $2\Delta(5^2D)$ state an inverted fine structure splitting of around -0.4 cm^{-1} was observed for all vibrational states which is in good agreement with the value predicted from the inverted fine structure splitting of the 5^2D state of the K atom. Up to now, the interatomic potentials of the higher excited 2Λ states could not be determined from our spectroscopic results as numerous avoided crossings between different potential curves are expected leading to large deviations from the usual ladder of vibrational energies.

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WG08 15 min 4:22

OBSERVATION OF RYDBERG STATES AND AUTOIONIZATION RESONANCES BY HIGH RESOLUTION ALL-OPTICAL TRIPLE RESONANCE SPECTROSCOPY, C. C. TSAI, J. T. BAHNS AND W. C. STWALLEY

Na_2 Rydberg states have been observed for $10 \leq n \leq 119$ and $0 \leq J \leq 9$ using high resolution all-optical triple resonance spectroscopy and an ultrasensitive ionization detector¹. Three cw single mode tunable ring dye/Ti:sapphire lasers (linewidth $< 0.5\text{ MHz}$) were used to reach the singlet ungerade Rydberg states of Na_2 .

$$n l \ ^1\Lambda_u^{(\pm)}(0, J) \xleftarrow{L_3} 3^1\Sigma_g^+(0, J') \xleftarrow{L_2} A^1\Sigma_u^+(1, J'') \xleftarrow{L_1} X^1\Sigma_g^+(1, J''').$$

The ionization potential (IP) of Na_2 was estimated by extrapolation to be $39478.75 \pm 0.04\text{ cm}^{-1}$. This implies that the dissociation energy of the molecular ion $D_e(\text{Na}_2^+ X^2\Sigma_g^+)$ is $7973.83 \pm 0.12\text{ cm}^{-1}$. Four series, $np^1\Sigma_u^+$, $np^1\Pi_u$, $nf^1\Sigma_u^+$ and $nf^1\Pi_u$, were found and rovibrational interactions, l -uncoupling, stroboscopic effects and Fano autoionization profiles were observed in the spectra.

1. C. C. Tsai, J. T. Bahns and W. C. Stwalley, Rev. Sci. Instrum. **63**, 5576 (1992).

WG09 15 min 4:39

CW PFOODR SPECTROSCOPY OF TRIPLET RYDBERG AND DOUBLY EXCITED STATES OF $^7\text{Li}_2$, A. YIANNPOULOU, B. JI, K. URBANSKI, LI LI, A.M. LYYRA, AND W.C. STWALLEY

By using CW perturbation-facilitated optical-optical double resonance (PFOODR) fluorescence excitation and resolved fluorescence spectroscopic techniques we have experimentally observed the $2^3\Sigma_g^+$, $3^3\Sigma_g^+$, $3^3\Pi_g$, $4^3\Sigma_g^+$ and $1^3\Delta_g$ Rydberg states and the $1^3\Sigma_g^-$ and $2^3\Pi_g$ doubly excited valence states. Perturbations of the $2^3\Pi_g \sim 1^3\Sigma_g^-$ system have been observed and the off-diagonal rotation-electronic perturbation parameter β has been determined. The hyperfine structure of most of the states has been resolved and characterized by ($b_{\beta J}$) or ($b_{\beta S}$) coupling case. Molecular constants and RKR potential energy curves have been obtained.

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WG10 15 min 4:56

THE NEWLY OBSERVED $5(4S,5D) \ ^1\Delta_g$ AND $5(4S,4D) \ ^1\Pi_g$ STATES OF K_2 STUDIED BY HIGH RESOLUTION OPTICAL OPTICAL DOUBLE RESONANCE SPECTROSCOPY, J. T. KIM, H. WANG, J. T. BAHNS, AND W. C. STWALLEY

Two low-lying Rydberg states of K_2 have been observed using high resolution optical optical double resonance spectroscopy. The absolute vibrational assignments have been done by comparing the excitation and resolved fluorescence intensities with the Franck Condon Factors calculated from Rydberg-Klein-Rees potential curves derived from fitted Dunham molecular constants. The atomic asymptotic assignments of the molecular Rydberg states have been done by comparing the molecular potential well separations with the correlated atomic energy separations. Bonding and antibonding characteristics of $^1\Delta_g$ and $^1\Pi_g$ states will be discussed.

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WH01 15 min 1:30

PHOTODISSOCIATION ELECTRONIC SPECTROSCOPY OF Mg^+ -RG COMPLEXES

J.S. Pilgrim, C.S. Yeh, K.R. Berry, and M.A. Duncan

The Mg^+ -rare gas diatomics (Ar, Kr, and Xe) are produced by laser vaporization in a pulsed molecular beam. Resonance Enhanced Photodissociation Spectroscopy (REPD) is used to obtain electronic spectra for these diatomics in a reflectron time-of-flight mass spectrometer. The chromophore for the electronic transition is the $\text{Mg}^+ 2\text{P} \leftarrow 2\text{S}$ atomic transition at 280 nm. The excited electronic states of the diatomics correlating to the 2P state of the atom are 2Π (observed) and 2Σ (not observed). Extensive vibronic spectra are obtained for these species with the origins or first members all progressively red-shifted as one descends the rare gas group. Least-squares fits to the standard form for an anharmonic oscillator give ω_e 's of 272, 258, and 258 cm^{-1} for Mg^+ -Ar, Kr, Xe respectively. Birge-Sponer extrapolations determine the 2Π bond energies to be 5550, 7130, and 11030 cm^{-1} for these species. Conservation of energy allows determination of the ground state bond energies of 1280, 1920, and 4180 cm^{-1} . The excited 2Π state in these molecules is split into spin-orbit states where $\Omega = 1/2$ and $3/2$. The spin-orbit splitting is found to be 77, 143, and 270 cm^{-1} for Mg^+ -Ar, Kr, Xe. The magnitudes of these spin-orbit splittings indicate very interesting phenomena in the excited state.

1. J.S. Pilgrim, C.S. Yeh, and M.A. Duncan, Chem. Phys. Lett. **210**, 322 (1993).
2. J.S. Pilgrim, C.S. Yeh, K.R. Berry, and M.A. Duncan, J. Chem. Phys. submitted

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WH02 15 min 1:47

PHOTODISSOCIATION SPECTROSCOPY OF Mg^+ - N_2 , D. L. Robbins, L. R. Brock, J. S. Pilgrim, and M. A. Duncan*

Electronic spectra for the ion-molecule complex, Mg^+-N_2 , is obtained via resonance enhanced photodissociation in a pulsed supersonic nozzle cluster source.¹ Mass selection occurs prior to photodissociation in a reflectron time-of-flight mass spectrometer. Bonding in this complex is expected to be predominantly charge quadrupole favoring a linear geometry. The spectra is red-shifted $> 10,000 \text{ cm}^{-1}$ from the atomic $\text{Mg}^+ 2\text{P} \leftarrow 2\text{S}$ transition and is assigned to $2\Pi \leftarrow 2\Sigma$. Six members of a progression of doublets with $\Delta G_{v'} + \frac{1}{2} \sim 1000 \text{ cm}^{-1}$ are observed. Multiplet bands in combination with each doublet band are assigned to the bending progression with $\Delta G_{\frac{1}{2}}' \sim 250 \text{ cm}^{-1}$. The large electronic red-shift and blue shading of observed peaks indicates a stronger and shorter bond in the 2Π excited state. Observation of spin-orbit coupling and Renner-Teller splitting of the bending progression agree with the expected linear geometry. This work is enhanced by *ab initio* calculations by Maitre and Bauschlicher² providing predictions of the electronic transition energies, vibrational constants, bond lengths, and dissociation energies.

1. D. L. Robbins, L. R. Brock, J. S. Pilgrim, and M. A. Duncan, (in preparation)
2. P. Maitre and C. Bauschlicher (private communications)

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WH03 15 min 2:04

ELECTROSTATIC INTERACTIONS IN THE IONIC AND VAN DER WAALS COMPLEXES, DIRECT APPROACH.

SERGEY I. PANOV AND TERRY A. MILLER

The analysis of spectroscopic data is one way to construct molecular potential energy curves, but the result of such a construction is always limited to the part of the potential surface probed by the observed transitions. In many cases a Morse potential closely approximates the real potential and is sufficient, for example, to estimate dissociation energies. But in the general case such an extrapolation should employ some long-range bonding model. Because spectroscopic data are not strongly affected by the inner-wall part of potential, the Hamiltonian can be written as a sum of an empirical repulsion term and the attractive electrostatic interaction term that is usually expressed in terms of the polarizabilities, hyperpolarizabilities, etc. However this approach has problems if there is a need to treat excited states with unknown polarizabilities; if electrostatic interaction induces significant changes in the molecular electronic eigenfunctions; or if there are more than two molecules in the complex. A direct, not perturbation theory based, approach is formulated and tested on the spectroscopic data of simple ionic complexes.

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WH04 15 min 2:21

ROTATIONAL AND NUCLEAR HYPERFINE STRUCTURE IN THE ELECTRONIC SPECTRUM OF CuCl_2
M.P.BARNES AND J.M.BROWN

We have recorded the electronic spectrum of copper dichloride, CuCl_2 , between 590 and 660nm in the gas phase. The sample was prepared at low temperatures using a free jet expansion from a heated nozzle. Under these conditions, rotational and even nuclear hyperfine structure was resolved. Many of the bands have been analysed in detail. Most of these involve the dominant isotope, $^{63}\text{Cu}^{35}\text{Cl}_2$, but we have identified bands attributable to all six possible isotopomers. The parallel rotational structure of a linear molecule is shown by all the bands, consistent with an electronic $^2\Pi_u - ^2\Pi_g$ transition, in agreement with *ab initio* calculations.

The majority of the bands studied are believed to involve the molecule in its ground vibrational state and are assigned as $^2\Pi_{3/2} - ^2\Pi_{3/2}$. From the lower state rotational constant for $\text{Cu}^{35}\text{Cl}_2$, the Cu - Cl bond length is calculated at $r_0'' = 0.203\,614(26)\text{nm}$. The vibrational structure in the region studied is very complicated and no detailed vibrational assignments have yet been made. Effort is being devoted towards identifying the (0,0) band of the electronic transition.

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WH05 10 min 2:38

OBSERVATION AND ANALYSIS OF THE TRIPLET-TRIPLET TRANSITION OF AlCl USING FTS

R.J. BRETT, K. I. MAHONEY, AND C. WELDON MATHEWS

The high resolution emission spectrum of the triplet-triplet transition of AlCl near $18\,000\text{ cm}^{-1}$ has been recorded with a Bruker IFS 120HR Fourier Transform Spectrometer. This system has been analyzed by Mahieu, et al¹ as a $^3\Delta - ^3\Pi$ transition, in contrast to previous interpretations as a $^3\Sigma^+ - ^3\Pi$ transition. The present data offer some improvement in resolution and considerable improvement in data on relative intensities of the transitions. This data permit us to provide a better contrast of the two alternative assignments and to determine an improved set of molecular constants for the upper state.

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1. E. Mahieu, I. DuBois, and H. Bredohl, J. Molec. Spectrosc. **138**, 264 (1989)

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WH06 10 min 2:50

THE A $^1\Pi - X^1\Sigma^+$ TRANSITION OF ALUMINUM MONOBROMIDE REVISITED
P. E. FLEMING AND C. WELDON MATHEWS

The two most recent reports^{1,2} of the A $^1\Pi - X^1\Sigma^+$ transition of AlBr show remarkable agreement in many of the measured line positions. Nevertheless, there are some significant differences in some of the derived constants. The present paper addresses some of these differences.

The spectrum has been recorded in emission in the region 2700 - 2800 Å using a Bruker IFS 120 HR Fourier transform spectrometer at a resolution of 0.03 cm⁻¹. These results permit comparison to photographic data while allowing for the numerous advantages of digital data collection common to Fourier transform spectroscopy. The results are in good agreement with previously reports for the 0-0 band. The 1-1 band, on the other hand, demonstrates some of the discrepancies previously noted. Results will also be presented on further refinements of assignments for other bands in the system.

1. W. B. Griffith and C. W. Mathews, J. Molec. Spectrosc. **104**, 347-352 (1984)
2. H. Bredohl, I. Dubois, E. Mahieu and F. Melen, J. Molec. Spectrosc. **145**, 12-17 (1991)

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WH07 15 min 3:02

UV SPECTROSCOPIC STUDIES OF PHOTOEXCITATION TO XeCl(B) AND XeF(B) STATES,
E.B. GORDON, V.G. EGOROV, S.E. NALIVAICO, V.S. PAVLENKO, AND O.S. RZHEVSKY

The XeCl(B) excitation spectrum resulting from photoabsorption, $XeCl(B, v' \leftarrow X, v'')$, and photoassociation, $Xe + Cl \rightarrow XeCl(B, v')$, processes as well as the XeF(B) excitation spectrum are obtained over the spectral ranges of 276..315 nm and 335..360 nm respectively. The double-pulse technique was applied, when the dissociation of halogen molecules by the pulse of the excimer XeCl-laser was followed by the delayed excitation pulse of the tunable dye laser. By measuring the XeCl(B) excitation intensity dependences on Xe pressure with a dissociating pulse and in the absence of that the contribution of photoassociative free-bound transitions was determined experimentally. Thus the rate constant of photoassociation, treated as a termolecular (two colliding atoms and a photon) process was estimated to be as high as $1 \cdot 10^{-28} \text{ cm}^6 \text{ s}^{-1}$ at the wavelength of 308 nm. The method for excitation spectrum calculations taking properly into account bound-bound and free-bound transitions contributions is developed. The XeCl(B) and XeF(B) excitation spectra are computed and for XeCl the absolute values of the photoabsorption cross-section and the photoassociation rate constant are calculated with at maxima at $\lambda \approx 308 \text{ nm}$ these values being $1.2 \cdot 10^{-16} \text{ cm}^2$ and $4.3 \cdot 10^{-28} \text{ cm}^6 \text{ s}^{-1}$ respectively.

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INTERMISSION

WH08 15 min 3:40
THE SINGLET-TRIPLET TRANSITION IN H_2CSe : CASE (AB) COUPLING IN THE TRIPLET STATE OF A POLYATOMIC MOLECULE

Dennis J. Clouthier, D.-L. Joo, R. H. Judge, and D. C. Moule

High resolution laser excitation spectra of the $\tilde{a}^3A_2 - \tilde{X}^1A_1$ band system of H_2CSe will be presented. Rotational analysis shows that the majority of the bands are *A*-type with no evidence of spin-splittings. However, the Zeeman effect on these bands is very pronounced in contrast to minimal effects on the corresponding $S_1 - S_0$ lines in the same vicinity. On the basis of *ab initio* predictions of the zero field splittings in the triplet state and a rotational analysis of the vibronically induced 4_0^1 band, for which all three components have been detected, we have concluded that the triplet state corresponds to case (ab) type I, in which one of the spin components is far removed from the other two. The triplet state energy level structure of this highly unusual case will be discussed.

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Address of Moule: Department of Chemistry, Brock University, St. Catharines, Ont., Canada L2S 3A1

WH09 10 min 3:57
THEORY AND APPLICATION OF THE SPIN-ROTATION HAMILTONIAN IN A CASE (A) BASIS TO THE SINGLET-TRIPLET BANDS OF SELENOFORMALDEHYDE

R. H. Judge, D.-L. Joo, Dennis J. Clouthier, and D. C. Moule

The triplet state spin-rotation Hamiltonian in a case (a) basis has been extended to include the effects of rotational centrifugal distortion. A general least squares and band contour program has been written that allows the use of case (a) and case (b) limit quantum numbers for molecules that fall into the intermediate [case (ab)] coupling schemes. The application of this program to the rotational analysis of the singlet-triplet bands of selenoformaldehyde will be discussed.

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WH10 15 min 4:09

Ni₂ REVISITED: REASSIGNMENT OF THE GROUND ELECTRONIC STATE IN AGREEMENT WITH LIGAND FIELD AND *ab initio* RESULTS, J. C. PINEGAR, J. D. LANGENBERG, C. A. ARRINGTON, E. M. SPAIN, AND M. D. MORSE

Resonant two-photon ionization spectroscopy was used to study Ni₂ produced by laser vaporization of a nickel target in the throat of a supersonic nozzle using argon as a carrier gas. Spectral regions previously investigated using helium as a carrier gas were reinvestigated, and the improved cooling achieved in this study was found to suppress transitions arising from an $\Omega = 4$ state that had been thought to be the ground state. Seven new vibronic progressions were assigned, with spectroscopic constants determined for the ground and excited states. The predissociation threshold in Ni₂ was reinvestigated, and a revised value for the binding energy is given as $D_0^{\circ}(\text{Ni}_2) = 2.042 \pm 0.002$ eV. The ionization energy of Ni₂ was found to be 7.430 ± 0.025 eV, and from this value and the revised binding energy of the neutral, the binding energy of the cation was calculated to be $D_0^{\circ}(\text{Ni}_2^+) = 2.245 \pm 0.025$ eV. Twenty bands were rotationally resolved, all originating from a lower state of $\Omega = 0_g^+$ or 0_u^- (which are indistinguishable in our experiments). We argue that this is the true ground state, in agreement with ligand field and *ab initio* theoretical studies. A weighted average of the B" values obtained from the rotational analyses yielded a ground state bond length of 2.1542 ± 0.0003 Å for ⁵⁸Ni₂.

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WH11 15 min 4:26

PHOTODISSOCIATION MEASUREMENTS OF BOND DISSOCIATION ENERGIES: Ti₂⁺, V₂⁺, Co₂⁺, AND Co₃⁺, LARRY M. RUSSON, SCOTT A. HEIDECKE, MICHELLE K. BIRKE, J. CONCEICAO, MICHAEL D. MORSE AND P. B. ARMENTROUT

The bond dissociation energies of Ti₂⁺, V₂⁺, Co₂⁺, and Co₃⁺ have been measured from the sudden onset of predissociation in the photodissociation spectra of these molecules, yielding values of $D_0^{\circ}(\text{Ti}_2^+) = 2.435 \pm 0.002$ eV, $D_0^{\circ}(\text{V}_2^+) = 3.140 \pm 0.002$ eV, $D_0^{\circ}(\text{Co}_2^+) = 2.765 \pm 0.001$ eV, and $D_0^{\circ}(\text{Co}_3^+) = 2.087 \pm 0.002$ eV. These values are in good agreement with values previously determined from collision-induced dissociation experiments. General criteria for the interpretation of predissociation thresholds as bond dissociation energies and periodic trends in the bonding of the 3d transition metal diatomic neutrals and monocations are discussed.

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WH12 10 min 4:43

PHOTODISSOCIATION MEASUREMENTS OF THE BOND DISSOCIATION ENERGIES OF TiZr, TiNb, AND VZr, JON D. LANGENBERG AND MICHAEL D. MORSE

The bond dissociation energies of TiZr, TiNb, and VZr have been determined by the abrupt onset of predissociation revealed in the resonant two-photon ionization spectra of these molecules. The dissociation energies are $D_0^{\circ}(\text{TiZr}) = 2.183 \pm 0.001$ eV, $D_0^{\circ}(\text{TiNb}) = 3.092 \pm 0.001$ eV, and $D_0^{\circ}(\text{VZr}) = 2.663 \pm 0.003$ eV. In addition to the requirements for interpreting predissociation thresholds as bond dissociation energies, periodic trends in the bonding of the 3d-4d mixed transition metal diatomics are discussed.

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WH13 15 min 4:55

THE $a^3\Sigma^+(u)(a_1^1(u)) \rightarrow X^1\Sigma^+(g)(XO^+(g))$ TRANSITIONS OF GROUP VA DIMERS,
R. BREIDOH, O. SHESTAKOV, K.D. SETZER, E. H. FINK, AND W. ZYRNICKI

Emission of the $a^3\Sigma^+(u)(a_1^1(u)) \rightarrow X^1\Sigma^+(g)(XO^+(g))$ transitions of Sb_2 , BiN , BiP , $BiAs$, $BiSb$, and Bi_2 has been observed in the near-infrared spectral region between 3800 and 11000 cm^{-1} from chemical reactions in fast flow systems. The spectra consisting of short sequences of red-degraded bands were measured at medium and high resolution with a Fourier-transform spectrometer. Vibrational analyses have yielded the following molecular constants of the $XO^+(g)$ and $a_1^1(u)$ states of the molecules (in cm^{-1}):

	T_e	ω_e'	$\omega_e x_e'$	ω_e''	$\omega_e x_e''$
Sb_2	9474.29	205.72	0.554	269.43	0.548
BiN	10144.6	501.67	4.713	736.53	4.802
BiP	9694.75	305.92	1.574	430.46	1.584
$BiAs$	8340.07	205.37	0.702	283.40	0.752
$BiSb$	7059.65	164.12	0.433	219.39	0.498
Bi_2	5509.62	133.79	0.304	173.03	0.375

Other new emission systems of BiN have been assigned to the transitions $b^5\Sigma^+(b_1^0) \rightarrow X^1\Sigma^+(XO^+)$ and $b^5\Sigma^+(b_1^0) \rightarrow a^3\Sigma^+(a_1^1)$. The spectra of BiN , BiP , $BiAs$ and Bi_2 have been measured at high resolution and accurate molecular constants of the states have been deduced.

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Address of Zyrnicki: Institute of Inorganic Chemistry and Metallurgy of Rare Elements, Technical University of Wrocław, 50-370 Wrocław, Poland

WH14 10 min 5:12

ROTATION-ELECTRONIC DEPERTURBATION ANALYSIS OF THE $4f6s$ CONFIGURATIONAL STATES OF CeO ,
L. A. KALEDIN, J. E. McCORD, AND M.C. HEAVEN

Rotation-electronic interactions between states of the $4f6s$ configuration mediated by the operator $-B(R)(\hat{J}_+ \cdot \hat{J}_+ + \hat{J}_- \cdot \hat{J}_-)$ have been calculated. We have used second-order perturbation theory to account for the effect of heterogeneous interactions on the rotation constants. Eigenvectors from the ligand field theory calculation were used to evaluate the $\langle e, \Omega | \hat{J}_+^2 | e', \Omega \pm 1 \rangle$ terms. The comparison of experimentally determined¹ and calculated rotational constants (in cm^{-1}) are presented in the Table:

State	T_0	$B_0(\text{exp.})$	$B_0(\text{cal.})$	δB_0	State	T_0	$B_0(\text{exp.})$	$B_0(\text{cal.})$	δB_0
U_{30^+}	4457.97(1)	0.36765(2)e	0.3658	0.0019	T_{10^-}	3818.79(1)	0.38145(6)f	0.3737	0.0078
U_{10^+}	1925.33(1)	0.4003(2)e	0.4008	-0.0005	V_{10^-}	1678.63(1)	0.357851(1)f	0.3573	0.0006
U_{21}	4134.05(1)	0.35238(4)e 0.36211(1)f	0.3535 0.3644	-0.0011 -0.0023	V_{41}	3634.96(1)	0.36562(2)e 0.34206(4)f	0.3612 0.3424	0.0044 -0.0003
V_{21}	1875.26(4)	0.3183(2)e 0.36142(1)f	0.3171 0.3610	0.0012 0.0004	W_{11}	812.67(1)	0.35729(6)e 0.35678(9)f	0.3567 0.3562	0.0006 0.0006
V_{32}	3462.16(1)	0.35379(2)	0.3554	-0.0016	W_{42}	2771.28(1)	0.36015(1)	0.3561	0.0041
W_{22}	911.79(5)	0.3622(3)	0.3582	0.0040	X_{12}	0.0	0.35454(1)	0.3572	-0.0027
W_{33}	2618.42(1)	0.35772(3)	0.3580	-0.0003	X_{33}	2142.55(1)	0.35660(1)	0.3580	-0.0014
X_{23}	82.30(1)	0.35696(1)	0.3580	-0.0010	X_{34}	2041.98(1)	0.35327(1)	0.3569	-0.0036

The calculation was performed with fitted parameters (in cm^{-1}) for the $4f6s$ configuration of CeO : $G_3(4f,6s)=295$; $\zeta_{4f}=596$; $B_0^2(4f,4f)=3356$; $B_0^4(4f,4f)=1541$; $B_0^6(4f,4f)=127$; $B_0=0.358$. This latter value correspond to $r_0=1.811$ Å.

1. L.A. Kaledin, J.E. McCord, and M.C. Heaven *J. Mol. Spectrosc.* **158**, 58 (1993).

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RA01 30 min 8:30

MQDT AND THE DOUBLE MINIMUM STATES OF H_2 : BORN-OPPENHEIMER DOES NOT WORK HERE!
STEPHEN ROSS AND CHRISTIAN JUNGEN

The rovibronic structure of the double minimum states of H_2 exhibits the effects of strong interactions. These interactions couple rotational, vibrational, and electronic motion, and are of such a magnitude that the Born-Oppenheimer picture is not even approximately correct. In fact, predictions for vibronic energies based on the straightforward solution of the one dimensional Schrodinger equation on the Born-Oppenheimer potential energy curves disagree with experiment by hundreds of wavenumber units.

Two theoretical approaches have been used to study the rovibronic structure of this fundamental system. Dressler and co-workers have calculated the adiabatic corrections to the Born-Oppenheimer potential energy curves and the non-adiabatic interaction functions between the lower $^1\Sigma_g^+$ Rydberg states. These results they then combine into a coupled equations treatment of the rovibronic structure of the related states. The results they obtain using this "traditional" approach reproduce the experimental rovibronic energies of the lower Rydberg states to within several cm^{-1} .

Our approach has been to study the same states using scattering theory. Multichannel Quantum Defect Theory (MQDT) is a version of scattering theory ideally suited to the study of such systems. In MQDT the concept of individual states is replaced by that of "channels". A channel consists of an entire Rydberg series and the continuum lying above it. By carefully determining the channels and their interactions a simple picture of a small number of interacting channels is thus sufficient to describe the entire *infinite* set of interacting states. MQDT thus avoids having to consider this infinity of mutually interacting states individually, while still accounting for the effects of their interaction.

In this talk the basic ideas of MQDT will be explained, with particular reference to our work on the double minimum states of H_2 . The rovibronic energies we obtain are of similar quality to those of Dressler and co-workers from the more traditional technique. We plan to extend our technique to progressively higher states and eventually into the continuum, which will allow us to provide a single unified treatment of both bound and continuum states, including the possibility of determining cross sections for such processes as dissociative recombination and photoionization.

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RA02 10 min 9:05

DIFFERENCE FREQUENCY LASER SPECTROSCOPY OF THE 5g-4f RYDBERG TRANSITIONS OF H_2
D. Uy, C.M. Gabrys, and T. Oka

In our search for the elusive spectrum of CH_5^+ in a methane-hydrogen discharge, we have found many strong negative-ion-shaped absorption lines in the 2500 cm^{-1} region. The large linewidth and the fact that it appears in a pure H_2 discharge confirms that it is a hydrogenic species. We compared the frequencies with those from two of the more recent studies^{1,2} of the 5g-4f spectra of H_2 and saw that, indeed, they belonged to H_2 . However, we were able to obtain about twice as many lines than the previous works, owing to the greater sensitivity achievable in our spectrometer. The analysis is currently in progress, being undertaken primarily by Dr. J.K.G. Watson.

1. Ch. Jungen, I. Dabrowski, G. Herzberg, M. Vervloet. *J. Chem. Phys.* **93**, 2289, 1990.
2. P.B. Davies, M.A. Guest, R.J. Stickland. *J. Chem. Phys.* **93**, 5417, 1990.

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RA03 15 min 9:17

VACUUM ULTRAVIOLET FLUORESCENCE DETECTION OF TWO-PHOTON EXCITATION SPECTRA OF I_2 RYDBERG STATES, B. D. RAFFERTY, L. P. GOLD, AND R. A. BERNHEIM

Vacuum ultraviolet fluorescence of iodine has been used to detect excitations through the 73394 cm^{-1} to 60150 cm^{-1} energy range. Eleven vibrational progressions corresponding to *gerade* Rydberg states of molecular iodine are identified. Twenty-two atomic LIF transitions following photodissociation are also identified. Combining and comparing these results with multiphoton ionization data¹ provides a better characterization of the *gerade* Rydberg states and new insight into the predissociation and photodissociation processes of the iodine molecule.

1. R. J. Donovan, R. V. Flood, K. P. Lawley, A. J. Yencha, and T. Ridley, *Chem. Phys.* **164**, 439 (1992).

Address of Rafferty, Gold, and Bernheim: Department of Chemistry, The Pennsylvania State University, University Park, PA 16802.

RA04 15 min 9:34

Theoretical Studies of the Rydberg State Predissociation of Methyl Iodide

H. Guo^a and A. H. Zewail^b

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The predissociation dynamics of several Rydberg states of methyl iodide are studied theoretically, pertinent to a recent femtosecond pump-probe experiment¹. The theoretical model involves two active modes in the predissociation, i.e. the C-I stretch and C-H₃ stretch. The quantal molecular dynamics on two-dimensional model potential energy surfaces show that the initial dynamics involves non-adiabatic transitions from the Rydberg state to the dissociative state along a vibrational mode involving the light atoms. Subsequent dynamics on the dissociative state lead to the C-I bond cleavage. The theoretical calculations reproduced not only the experimental decay transients, but also the large isotope effect and mode specificity in the predissociation rate. The two-dimensional dynamics underscore the importance of multidimensionality in the predissociation dynamics of these Rydberg states.

1. M. H. M. Janssen, M. Dantus, H. Guo and A. H. Zewail, *Chem. Phys. Lett.*, **214**, 281 (1993).

RA'01 15 min 10:00

Applications of Two-Color Resonant Four-Wave Mixing to SEP Spectroscopy

J. R. DUNLOP, J. D. TOBIASON, AND E. A. ROHLFING

Two-color resonant four-wave mixing (RFWM) derives its resonant enhancement from two distinct molecular resonances and is thus applicable to a variety of double-resonance spectroscopies. In this talk, we focus on the use of two-color RFWM to obtain background-free stimulated emission pumping (SEP) spectra. Two schemes are utilized: $\omega_P - \omega_P + \omega_D = \omega_S$ and $\omega_P - \omega_D + \omega_D = \omega_S$, where ω_P , ω_D , and ω_S denote the SEP PUMP, SEP DUMP, and RFWM signal frequencies, respectively. The first scheme is commonly interpreted as a laser-induced grating in the excited state while the second scheme can be thought of as a Raman coherence between two ground-state levels separated in energy by $\omega_P - \omega_D$. Both schemes can be interpreted in the weak-field limit using diagrammatic perturbation theory. We apply these RFWM-SEP techniques to transient molecules cooled in a free jet expansion; examples include the $\tilde{A}^1B_2 - \tilde{X}^1A_1$ system of SiC_2 , the $\tilde{A}^1\Pi_u - \tilde{X}^1\Sigma_g^+$ system of C_3 , and the $\tilde{B}^2A' - \tilde{X}^2A'$ system of the HCO radical. We shall discuss the practical advantages and disadvantages of the RFWM-SEP approaches, with respect to each other and to the conventional technique of SEP detection via fluorescence depletion, the effects of beam geometry and relative polarizations on relative rotational line intensities, and the lineshape functions for tuning the DUMP frequency, ω_D .

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RA'02 15 min 10:17

**SEP Spectroscopy of the $\tilde{B}^2A' - \tilde{X}^2A'$ System of Jet-cooled HCO and DCO:
Vibrational Structure of the \tilde{X}^2A' State Near and Above Dissociation**

J. R. DUNLOP, J. D. TOBIASON, AND E. A. ROHLFING

The formyl radical, HCO, is an important combustion intermediate that has been studied by a variety of spectroscopic techniques. Despite this, the ground-state potential energy surface and vibrational structure near the dissociation barrier are not fully understood. We use stimulated emission pumping (SEP), via either two-color resonant four-wave mixing (RFWM) or fluorescence depletion, to observe a wide range of vibrational levels in the \tilde{X}^2A' state of HCO and DCO. The combination of the two techniques provides determinations of energies and widths of vibrational states above and below the threshold for dissociation into H+CO. Spectra of \tilde{X}^2A' state C-O stretch, bend and combination levels obtained by pumping the $\tilde{B}^2A' - \tilde{X}^2A'$ electronic origin confirm the applicability of RFWM-SEP and yield new results. Spectra involving the C-H stretch in the \tilde{X}^2A' state, obtained by pumping one quanta of C-H stretch in the \tilde{B}^2A' state, provide new experimental data showing the enhancement in dissociation rate upon C-H excitation. The C-H stretch and bending levels show interesting mode specific dissociation rates that are compared to recent theoretical calculations. In contrast to HCO, only a small spectroscopic data set exists for DCO. Results for DCO are among the first experimental data to probe its ground-state vibrational structure. Both sets of results will be helpful in a more rigorous determination of the potential energy surface for the \tilde{X}^2A' state.

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RA'03 15 min 10:34**TUNABLE VACUUM ULTRAVIOLET PHOFEX SPECTROSCOPY OF OCS**
C. D. PIBEL, K. OHDE, AND K. YAMANOUCHI

The photofragment excitation (PHOFEX) spectrum of jet-cooled OCS has been measured in the vacuum ultraviolet (VUV) region between 140 - 160 nm. The electronically excited S (¹S) photoproduct, produced by tunable VUV laser photolysis, was detected by laser induced fluorescence via the ³D₁^o - ¹S transition. The observed PHOFEX spectrum is better resolved than previous room-temperature and jet-cooled absorption spectra, and new features are observed. The dynamics of the photodissociation will be discussed using the measured PHOFEX spectrum, as well as the S (¹S) Doppler profiles.

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RA'04 15 min 10:51**SPECIFIC RATE CONSTANTS $k(E,J)$ OF NO₂ FROM LINEWIDTH MEASUREMENTS USING OPTICAL DOUBLE-RESONANCE SPECTROSCOPY IN A FREE JET**
B. Abel, H. Hamann, N. Lange, and J. Troe

Laser induced fluorescence detected optical V-type double resonance spectroscopy in a free jet has been employed to access and to assign rovibronic states of NO₂ above the dissociation threshold E_0 .

The measured homogeneous linewidths of isolated lines above the dissociation threshold have been converted into specific rate constants $k(E,J)$. The rate constants, its fluctuations, and its dependence on E and J will be discussed in terms of statistical theories.

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RA'05 15 min 11:08**OBSERVATION OF HIGHLY VIBRATIONALLY EXCITED $\tilde{X}^1\Sigma^+$ HCP BY STIMULATED EMISSION PUMPING SPECTROSCOPY, H. ISHIKAWA AND R.W. FIELD**

We have observed stimulated emission pumping (SEP) spectra of vibrationally excited $\tilde{X}^1\Sigma^+$ HCP via its \tilde{C}^1A' state. We measured high resolution SEP spectra of two thirds of the 22 500 cm⁻¹ - 23 200 cm⁻¹ region. Since the $\tilde{C} - \tilde{X}$ transition is a parallel one, only $l'' = 0$ levels are accessible by allowed transitions. When the P(J) line is used as a pump transition, the R(J-2) and P(J) lines appear in the spectrum. We used P(2), P(4), ..., P(10) lines as pump transitions. There, 20 vibrational levels were found. Among them, 17 levels have definitely a J = 0 level. This indicates that they are definitely $l'' = 0$ levels. In the previous SEP study via the \tilde{A}^1A'' state¹, only pure bend overtone levels were observed in this region. It is expected that there is one Franck-Condon bright series (0, 38, 0), (0, 36, 1), (0, 34, 2), ..., (0, 24, 7). Considering the level density, combination levels involving H atom radial motion must be excited. The B constants of these levels are in the range 0.63 cm⁻¹ - 0.76 cm⁻¹. Compared with the B constant in the vibrational ground state, 0.666 cm⁻¹, a B constant of more than 0.7 cm⁻¹ is so large as to be of diagnostic significance. The 4 levels which have B constant of more than 0.72 cm⁻¹ can be assigned as members of a similar (n, v, 0), (n, v-2, 1), ... series built on n ≠ 0 quanta of H—(CP) stretch. Detailed analysis will be presented.

1. Y.-T. Chen, D.M. Watt, R.W. Field and K.K. Lehmann, J. Chem. Phys. **93**, 2149 (1990).

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RA'06 15 min 11:25

ANALYSIS OF THE $3^1A'$ STATE OF HCP, B. RAJARAM, J. WANG, Y.T. CHEN, S.L. COY, AND R.W. FIELD

The predissociated $3^1A'$ state of HCP, whose origin is at $50642.18 \pm 09 \text{ cm}^{-1}$, has been observed for the first time in fluorescence-dip detected optical-optical double resonance spectra excited using selected single rovibronic levels of the A^1A'' state of HCP as intermediate level. The bending vibration (v_2) appears to be extremely anharmonic, with the spacings between successive members of the bending progression *increasing* for a given value of the K_a quantum number. A rapid increase in the A rotational constant with v_2 has also been observed, in combination with an increase in the ratio $\Delta E(1,0)/\Delta E(2,0)$ [where $\Delta E(i,j)$ is the spacing between the $K_a = i$ and j levels] from a value close to the value of 0.25 that is typical for an ideal bent molecule. This ratio would have a value close to 0.5 in the linear limit. These effects seem consistent with quasilinear and/or Renner-Teller behavior of the $3^1A'$ state. *Ab initio* calculations¹ suggest that the $3^1A'$ potential surface arises from a conical intersection between the lower component of the Renner-Teller split $n \leftarrow \pi^1I$ state and the quasilinear $\pi^{*2} \leftarrow \pi^2 2^1\Sigma^+$ state. The rotational and vibrational mode dependence of the linewidths (FWHM) of the OODR transitions and an analysis of the quasilinear/Renner-Teller behavior will be presented.

¹ S. P. Karna, P. J. Bruna, and F. Grein, *Canad. J. Phys.* **68**, 499 (1990).

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RA'07 15 min 11:42

THE FLUORESCENCE EXCITATION SPECTRA OF HCP AND DCP FROM 34000 CM^{-1} TO THE GROUND ELECTRONIC STATE DISSOCIATION THRESHOLD, M.A. MASON AND K.K. LEHMANN

As an extension of our previous work, the fluorescence excitation spectra of HCP and DCP cooled in a supersonic expansion has been recorded from 34000 cm^{-1} to the dissociation limit of the ground state. Once the dissociation limit of the ground electronic state was crossed, a sharp reduction in fluorescence quantum yield was detected that has allowed a precise determination of the ground state dissociation limit for both species. In this region, nearly four times the number of bands reported via absorption have been observed. In agreement with previous investigations, most of the bands lying below $\sim 38000 \text{ cm}^{-1}$ are characterized by a perpendicular transition moment and have been assigned to a single electronic state, the $\tilde{A}(^1A'')$ state. Attempts to model the \tilde{A} state bending progression as a two-dimensional harmonic oscillator will be discussed. Above 38000 cm^{-1} , the electronic spectrum becomes considerably more complex and many bands in this region remain unassigned. However, a series of bands characterized by a parallel transition moment can be readily distinguished from higher vibronic levels of the \tilde{A} state and have been assigned to the \tilde{C} state. The $0^0(K=0)$ band for the HCP \tilde{C} state lies at 38787 cm^{-1} with the $0^0(K=1)$ band lying 14 cm^{-1} above it. For the higher vibronic levels of the \tilde{C} state, the $K=1$ levels fall below the $K=0$ levels as expected if the \tilde{C} state were the lower Renner-Teller component of a $^1\Delta$ state.

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RA'08 10 min 11:59

HIGH-RESOLUTION INFRARED SPECTROSCOPY OF SrF

Pina Colarusso, B. Guo, K.Q. Zhang and P.F. Bernath

The infrared spectrum of gaseous SrF was recorded using a Bruker Fourier transform spectrometer. The thermal emission spectrum of SrF was obtained at 1550°C with a Si:B detector at a resolution of 0.01 cm⁻¹. Vibrational-rotational bands of the X²Σ⁺ ground state were observed in the region between 400-550 cm⁻¹. A rotational analysis of the spectrum will be presented.

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RB01 15 min 8:30

THE VIBRATIONAL ENERGY PATTERN IN PYRROLE

A. HELD AND M. HERMAN

We have recorded the absorption spectrum of pyrrole at high resolution with a Fourier transform interferometer, from the mid-infrared to the near-infrared ranges. Several bands are observed and tentatively assigned in this work. Most of the bands present resolved clusters of lines that can be rotationally assigned, as already performed for the $\Delta v=1$ and 3 N-H stretching vibrations^{1,2}. The results of the rotational analysis will be presented.

In addition, the results of experiments performed with a new long-slit jet apparatus coupled to the Fourier transform instrument will be reported, if successful by the time of the meeting.

1. M. Carlotti, G. Di Lonardo, G. Galloni and A. Trombetti, J. Chem. Soc. Faraday Discuss. **68**, 1473 (1972).

2. C. Douketis and J.P. Reilly, J. Chem. Phys. **96**, 3431 (1992).

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RB02 15 min 8:47

DETERMINATION OF THE SPECTROSCOPIC CONSTANTS OF A DARK VIBRATIONAL STATE: FERMI AND CORIOLIS PERTURBATIONS IN THE ν_2 BAND OF FORMYL CHLORIDE

Dennis J. Clouthier, D.-L. Joo, and A. J. Merer

The ν_2 (CO stretching) fundamental of the transient molecule formyl chloride, HCOCl, has been recorded at high resolution and rotationally analyzed. Numerous excited state perturbations occur throughout the band, caused mainly by $|\Delta K_a| = 2$ Fermi resonance and $|\Delta K_a| = 1$ Coriolis interactions with the $3^1 5^1$ vibrational state. Even though no "extra" lines resulting from the perturbations could be assigned, a complete analysis of the perturbed rotational structure has been possible. Accurate molecular constants for both the "bright" perturbed 2^1 state and the "dark" $3^1 5^1$ perturbing state have been obtained, using a Hamiltonian which includes both the Fermi and Coriolis interactions; only two interaction parameters are needed, one for each mechanism. Further perturbations at high K_a are assigned to Coriolis interactions with the $5^2 6^1$ level.

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RB03 10 min 9:04

VIBRATIONAL OVERTONE SPECTROSCOPY OF PYRIDINE AND FLUOROPYRIDINES

Joyce A. Overly and Deanne Snively

The visible vibrational spectra of gaseous pyridine, 3-fluoropyridine, and 2,6-difluoropyridine have been recorded up to $v=6$ using intracavity dye laser photoacoustic spectroscopy. The overtone spectrum of each compound shows a progression of two peaks at each vibrational level and in each case the two peaks, taken separately, fit well to a Birge-Sponer plot. Compared to the pyridine vibrational overtones, the peak maxima for 3-fluoropyridine and 2,6-difluoropyridine are blue-shifted by about $20v$ and $50v$ cm^{-1} , respectively, where v is the vibrational quantum number. In earlier local mode analyses^{1,2} of the liquid phase overtone spectrum of pyridine the two peaks were assigned to the $C_{\alpha}\text{-H}$ and $C_{\beta,\gamma}\text{-H}$ stretches. Our results are compared to this model and assignments are suggested for the overtone spectra of the substituted pyridines.

1. R. Bini, P. Foggi and R.G. Della Valle, *J. Phys. Chem.* **95**, 3027 (1991).
2. M. Katayama, K. Itaya, T. Nasu, J. Sakai, *J. Phys. Chem.* **95**, 10592 (1991).

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RB04 15 min 9:16

HIGH RESOLUTION STUDY OF THE ν_9 , ν_{10} , and ν_{11} BANDS OF CYCLOPROPANE- D_6 J. PLÍVA, A. VALENTIN, AND L. HENRY

The perpendicular infrared bands of the E' vibrations of C_3D_6 were measured on a large FT spectrometer at resolution approaching the Doppler limit. The unperturbed ν_{11} band provided the most extensive data yielding 867 combination differences for a determination of accurate ground state constants B_0 and D_J . These were combined with highly accurate values of C_0 - B_0 and D_{JK} recently determined by Bauder *et al.* from an FTMW measurement of the rotational spectrum: $B_0 = 0.4613514(4)$, $C_0 = 0.3182425(4)$, $D_J^0 = 3.7868(18) \times 10^{-7}$, $D_{JK}^0 = -3.7395(7) \times 10^{-7}$ (all in cm^{-1} units).

The ν_{10} band was found to have an appearance of a parallel band due to an accidental match of the values of $(Cf)_{10}$ and $B' - C'$. The ν_9 band exhibits a perturbation in its P-branches due to Fermi resonance with $2\nu_{14}^2$. Spectroscopic constants for the upper states ν_{11} , ν_{10} , ν_9 , and $2\nu_{14}^2$ obtained from a detailed rotational analysis of the three bands will be reported.

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RB05

15 min

9:33

HIGH RESOLUTION INFRARED SPECTROSCOPY AND ANALYSIS OF METHYLISOCYANIDE BANDS IN THE 1370-1560 cm^{-1} REGION, L. D. LE, J. PLÍVA, L. P. GOLD, C. HE, AND R. A. BERNHEIM

The region 1370-1560 cm^{-1} contains two fundamental bands: the strong perpendicular band of the doubly degenerate vibration ν_6 (species E) and the parallel band of the totally symmetric (A_1) vibration ν_3 . In addition, the $\nu_7 + \nu_8$ and $\nu_4 + 2\nu_8$ combination states also occur in this region. The two fundamentals interact strongly by a first order $J_{x,y}$ -Coriolis coupling while the E component of $\nu_7 + \nu_8$ is in Fermi resonance with ν_6 , and the A_1 and A_2 components of $\nu_7 + \nu_8$ are in Fermi resonance with the ν_3 fundamental. Also in evidence are an additional weaker anharmonic resonance of ν_6 with the $\nu_4 + 2\nu_8^2$ combination, as well as x,y-Coriolis-type and second-order rotational interactions which couple the various states. The interactions are incorporated into a 9×9 Hamiltonian matrix used for the upper states to adjust their spectroscopic constants yielding an overall standard deviation of the fit to all observed lines of 0.0015 cm^{-1} . Spectroscopic parameters for all the states involved and for their interactions will be reported.

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RB06

10 min

9:50

RAMAN AND INFRARED SPECTRA, CONFORMATIONAL STABILITY AND *AB INITIO* CALCULATIONS OF *TRANS*-1-FLUORO-2-BUTENE, D. T. Durig, Mengzhang Zhen and J. R. Durig

The Raman (3200 to 10 cm^{-1}) and infrared (3200 to 20 cm^{-1}) spectra of gaseous and solid *trans*-1-fluoro-2-butene, *trans*- $\text{CH}_3\text{HC}=\text{CHCH}_2\text{F}$, have been recorded. Additionally, the Raman spectrum of the liquid with qualitative depolarization data has also been obtained. Variable temperature studies have been carried out with the sample dissolved in xenon. These spectral data have been interpreted on the basis that the molecule exists in the fluid phases as a mixture of the synclinal (fluorine atom oriented *cis* to the double bond) and anticlinal (*gauche*) conformations. In the gaseous phase the synclinal conformer is more stable by $265 \pm 62 \text{ cm}^{-1}$ ($758 \pm 177 \text{ cal/mol}$) but in the liquid state the anticlinal conformer is more stable and the only conformer present in the solid state. *Ab initio* gradient calculations employing the RHF/3-21G*, RHF/6-31G* and MP2/6-31G* basis sets predict the synclinal conformer to be more stable.

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INTERMISSION

RB07 10 min 10:20

RAMAN AND INFRARED SPECTRA, CONFORMATIONAL STABILITY AND BARRIERS TO INTERNAL ROTATION OF 3-BROMO-2-METHYLPROPENE, Saadia Eltayeb, G. A. Guirgis and J. R. Durig

The Raman (3200 to 20 cm^{-1}) and infrared (3200 to 35 cm^{-1}) spectra of 3-bromo-2-methylpropene, $\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{CH}_2\text{Br}$, have been recorded for the gas and solid. Additionally, the Raman spectrum of the liquid has been recorded and qualitative depolarization values obtained. The fundamental asymmetric torsional mode for the *gauche* conformer is observed at 81.5 cm^{-1} with one excited state falling at a lower frequency but the asymmetric torsion is not observed for the higher energy *s-cis* conformer. Utilizing the *gauche* observed torsional frequencies, the *gauche* dihedral angle, the enthalpy difference between conformers, and the calculated torsional fundamental frequency for the *s-cis* conformer, the potential function governing the interconversion of the rotamers has been estimated. This potential function gives values of 170 cm^{-1} (486 cal/mol), 2659 cm^{-1} (7.60 kcal/mol), and 725 cm^{-1} (2.07 kcal/mol), for the *s-cis* to *gauche*, *gauche* to *gauche*, and *gauche* to *s-cis* barriers, respectively, and it is compared to that obtained with the RHF/STO-3G* basis set. From the methyl torsional frequency of 172 cm^{-1} for the *gauche* conformer, the threefold barrier of 695 cm^{-1} (1.99 kcal/mol) has been calculated for the methyl group. A complete vibrational assignment is proposed based on Raman depolarization data, group frequencies, and relative infrared and Raman intensities. The conformational energy difference and optimized geometries of both conformers have also been obtained from *ab initio* calculations.

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RB08 10 min 10:32

RAMAN AND INFRARED SPECTRA, CONFORMATIONAL STABILITY AND BARRIERS TO INTERNAL ROTATION OF TRIFLUOROACETYL ISOCYANATE, K. A. Krutules, G. A. Guirgis and J. R. Durig

The Raman (3100 to 10 cm^{-1}) and infrared (3100 to 30 cm^{-1}) spectra of trifluoroacetyl isocyanate, $\text{CF}_3\text{C}(\text{O})\text{NCO}$, have been recorded for the gas and solid. Additionally, the Raman spectrum of the liquid has been recorded and qualitative depolarization values obtained. The observed bands are assigned on the basis of the more stable *cis* conformer (isocyanate group *cis* to the carbonyl bond) and the less stable *trans* conformer in all three physical states. The potential function governing conformational interchange has been determined and the values of the potential constants are: $V_1 = 356 \pm 14$, $V_2 = 1865 \pm 60$, and $V_3 = 203 \pm 6 \text{ cm}^{-1}$. Variable temperature studies of the Raman spectrum of the liquid gives a ΔH of $236 \pm 30 \text{ cm}^{-1}$ ($675 \pm 86 \text{ cal/mol}$). A complete vibrational assignment is proposed for the *cis* conformer based on infrared band contours, Raman depolarization data, group frequencies, relative intensities, and normal coordinate calculations. Also, several of the fundamentals of the *trans* conformer have been assigned. The experimental conformational stability, barriers to internal rotation, structural parameters, and fundamental vibrational frequencies are compared with those obtained from *ab initio* gradient calculations.

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RB09 10 min 10:44**RAMAN SPECTRA AND CONFORMATIONAL STABILITY OF METHOXYDICHLOROPHOSPHINE, J. B. Robb, II and J. R. Durig**

The Raman spectra (3500 to 30 cm^{-1}) of gaseous and solid methoxydichlorophosphine, CH_3OPCl_2 , have been recorded and only the *trans* conformer (methyl group *trans* to the phosphorus lone pair) is present in either spectrum. Additionally, the far infrared spectrum of the gas has been recorded from 350 to 30 cm^{-1} at a resolution of 0.10 cm^{-1} . The fundamental asymmetric torsional mode has been observed at 120 cm^{-1} , and the frequency of the methyl torsional mode is estimated to be 58 cm^{-1} from a combination band. Estimates are given for the barriers for these internal torsional modes. A complete vibrational assignment is given for both the normal and d_3 -isotopomer. The fundamental vibrational frequencies and barriers to internal rotation which have been obtained experimentally are compared to those obtained from *ab initio* Hartree-Fock calculations employing the 3-21G* basis set. The structural parameters and relative conformer stabilities have been obtained with the RHF/6-31G* and MP2/6-31G* basis sets. From these calculations, the *gauche* conformer is estimated to be more than 4.0 kcal/mol less stable than the *trans* conformer which is consistent with the observation of only the *trans* conformer in the Raman spectrum of the gas at ambient temperature.

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RB10 10 min 10:56**CONFORMATIONAL STABILITY OF OXALYL CHLORIDE, J. E. Davis and J. R. Durig**

The Raman spectra (2000 to 10 cm^{-1}) of gaseous, liquid and solid oxalyl chloride, $(\text{CClO})_2$, have been recorded and the Raman spectrum of the liquid with qualitative depolarization values have been obtained. In addition to the six symmetry permitted Raman lines for the *trans* conformer, there are eight more Raman lines observed in the spectrum of the gas (ten for the liquid) which must be assigned to a second conformer. These data have been interpreted on the basis of a more stable *trans* rotamer and a high energy *gauche* conformer in equilibrium for the fluid phases. Assignments are provided for most of the fundamentals for the *gauche* conformer.

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RB11 15 min 11:08

ABSOLUTE INFRARED ABSORPTION INTENSITIES AND OPTICAL CONSTANTS OF THE NEAT LIQUIDS CH₃OH, CH₃OD, CD₃OH and CD₃OD, S.L. ZHANG AND J.E. BERTIE

The infrared absorption by four isotopic forms of neat liquid methanol has been measured by attenuated total reflection and transmission methods, as has been described for CH₃OH and CH₃OD^{1,2}. The measurements were converted to spectra of the real and imaginary refractive index, the optical constants, and then to spectra of the imaginary molar polarizability or its close relative the susceptibility. The absorption measurements are believed to be accurate to about 3%. The spectra of the different isotopic forms allow the contributions to the intensity from different vibrations to be separated with unusually high confidence, and we believe the integrated intensities of the different vibrations are known to a few percent. The integrated intensities and transition moments will be reported, the effect of isotope on the intensities will be noted, and the use of double harmonic theory to obtain dipole moment parameters for these liquid-phase molecules will be discussed.

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1. J.E. Bertie, S.L. Zhang, H.H. Eysel, S. Baluja and M.K. Ahmed, *Applied Spectroscopy* **47**, 1100 - 1114 (1993)
 2. J.E. Bertie and S.L. Zhang, *Applied Spectroscopy* **48**, 176 - 189 (1994)
-

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RB12 10 min 11:25

Step-Scan Time Resolution of the Photoluminescence of Porous Silicon, Thomas J. Tague Jr., Gunther Zachmann, and Manfred Reiche

Rapid-scan and step-scan time resolved Fourier transform techniques have been employed to monitor the photoluminescence of porous silicon. The 514 nm line of an argon ion laser was chopped and allowed to impinge on a porous silicon wafer. The resultant radiation, centered at 740 nm, was collected through an emission port of a Bruker model IFS 66 spectrometer. Rapid-scan measurements proved too slow to resolve the photoluminescence decay time, while step-scan measurements revealed a lifetime of 50 μ s.

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RB13 15 min 11:37

CRITICAL BEHAVIOUR OF THE ν_5 -LO(177 cm^{-1}) RAMAN MODE OF NH_4Br ,
H. YURTSEVEN

We have studied here the critical behaviour of the Raman frequencies for the ν_5 -LO(177 cm^{-1}) phonon mode of NH_4Br . We have analyzed our observed Raman frequencies for this mode which were obtained as a function of temperature near the λ point for zero pressure. Our analysis gives the value of $a' = -1/2$ for the critical exponent of the Raman frequency shifts below the λ transition temperature ($T_\lambda = 235\text{K}$, $P=0$). This exponent value may be considered as the renormalized Fisher exponent $a'_R = -a'/(1-a')$, which gives $a'_R = 1/3$ below T_λ . Since a linear variation with temperature between the specific heat and the Raman frequency shifts can be established in the vicinity of ammonium halides below T_λ , our exponent value can describe the critical behaviour of the specific heat in NH_4Br .

I.H. Yurtseven, J. Mol. Struct. 115, 173 (1984).

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RB14 15 min 11:54

SURFACE ENHANCED RAMAN SCATTERING USED AS AN *IN-SITU* ANALYTICAL METHOD FOR STUDIES OF POLYMER\METAL INTERFACE

Gendin Ji and Gi Xue

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The microstructure at the polymer-metal interface have been observed by the use of surface enhanced Raman scattering (SERS). SERS spectra are compared with the infrared reflection-adsorption spectra for adhesive coatings of polymer on metals. Results show that SERS is an effective *in-situ* analytical technique which is highly informative in that the authentic adsorption state and the microstructure of the first monolayer near the metal surface can be revealed with much less interference from the polymer bulk. The ring opening reaction of an epoxy resin on top of chemisorbed coupling agents has been observed by the use of surface enhanced Raman scattering.

References

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RC01 30 min 8:30

SPECTROSCOPY WITHOUT SPECTROMETER: THE ROVIBRONIC SPECTRA OF NiH, PdH, AND PtH

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The spectra of small, unsaturated transition metal compounds are generally complicated and, despite considerable progress in modern high-resolution laser spectroscopy, far from understood. One of the reasons for the complexity of these spectra is the presence of a multitude of low-lying molecular electronic states. These emerge from the energetic proximity of the nd^{i+2} , $nd^{i+1}(n+1)s^1$, and $nd^i(n+1)s^2$ configurations in transition metal atoms and the large number of ways in which their angular momenta can be coupled. Moreover, spin-orbit interaction causes heavy perturbations between the densely spaced electronic states.

Electronic structure calculations including spin-orbit and rotational coupling can be of considerable help in explaining and assigning these complex spectra. By starting off in a basis of electronic $\Lambda\Sigma$ eigenstates we avoid the computation of radial non-adiabatic coupling matrix elements caused by the spin-dependent parts of the relativistic Hamiltonian. Electron correlation is included by applying general purpose electronic structure codes. Spin-orbit and rotational interactions between the electronic states are accounted for in a second step. After a transformation of these off-diagonal potentials to a basis of unperturbed rovibronic functions the J -dependent coupling matrices are diagonalized. Eigenvalues obtained in this way can directly be compared with measured term values. Applications to the spectra of NiH, PdH, and PtH will be presented.

RC02 15 min 9:05

MOLECULAR INTEGRAL OF SPHERICAL GAUSSIAN AND ITS APPLICATION IN DIFFERENT MOLECULAR STATE GEOMETRIES, LUE-YUNG CHOW CHIU AND MOHAMMAD MOHARRERZADEH

The multicenter molecular integrals of the overlap, nuclear attraction, kinetic energy and two-electron Coulomb repulsion over the homogeneous solid harmonic spherical Gaussians $r^{2n+l}Y_{lm}(\theta\phi)\exp(-\alpha r^2)$ are integrated by expanding the function from one center to another. The expansion of the regular solid spherical harmonics $r^l Y_{lm}(\theta\phi)$ (and the irregular solid spherical harmonics $r^{-(l+1)} Y_{lm}(\theta\phi)$) about a displaced center is shown to be an irreducible tensor coupling of two solid spherical harmonic tensors; one refers to the displaced center and the other is made of the displacement vector. The Gaussian exponentials are expanded at the displaced center through the modified plane wave expansion. The overlap integral involving non-homogeneous solid harmonic spherical Gaussians $r^{(2n+l)+1} Y_{lm}(\theta\phi)\exp(-\alpha r^2)$ has also been integrated. The results obtained are in *simple analytical expressions*. Within these expressions all the magnetic quantum numbers appear only in two places: in the Clebsch-Gordan coefficients and in the spherical harmonics of the internuclear vector (referring to an arbitrary frame of reference). Molecular geometry of different states can be obtained by optimizing bond distances and bond angles which appear explicitly in each integral expression.

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RC03 15 min 9:22

Active Space Requirements for State Specific MRPT and MRAQCC Methods

Galen F. Gawboy, and Isaiah Shavitt

The recent formulation of State Specific Multireference Perturbation Theory and the Multireference Averaged Quadratic Coupled Cluster methods allows for treatment of dynamic and non-dynamic electron correlation which is approximately size consistent. The focus of the present work is to explore the active space requirements for MRACPF, MRAQCC, MRCISD, and MRPT methods. Spectroscopic constants, excitation energies, and electron affinities have been computed with a wide range of active spaces for the chromophore involving the $C_2 X^1\Sigma_g^+$, $C_2 a^3\Pi_u$, $C_2^- X^2\Sigma_g^+$, $C_2^- A^2\Pi_u$, and the $C_2^- B^2\Sigma_u^+$ states.

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RC04 15 min 9:39

AB INITIO COMPUTATIONS OF OF SEMIEMPIRICAL π -ELECTRON METHODS: STRUCTURE AND TRANSFERABILITY OF PARAMETERS

Charles H. Martin and Karl F. Freed

The effective valence shell Hamiltonian (\mathcal{H}^v) method is used to compute the true π -electron parameters of a number of small, conjugated molecules. These true parameters are used to test several fundamental assumptions of semiempirical π -electron, such as the zero-differential-overlap (ZDO) approximation, the transferability of parameters, and the role of three- and four-electron interactions. The true π -electron parameters display remarkable transferability between different molecules, and corrections to the ZDO approximation are evident. The role of three- and four-electron parameters are interpreted for the low-lying spectra.

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RC05 15 min 9:56

FITS TO A NEWLY CALCULATED POTENTIAL SURFACE FOR THE REACTION $Li + FH \rightarrow LiF + H$.

P. PENDERGAST AND E. F. HAYES

The reaction $Li + FH \rightarrow LiF + H$ is a prototype of alkali plus hydrogen halide reactions. Despite this fact, only semi-empirical and a qualitatively accurate *ab initio* potential energy surfaces have been calculated. The previous *ab initio* surface was significantly modified for fitting because its stationary points were not in agreement with experiment. But now a new and accurate potential energy surface has been calculated. Because it is the calculated PES from which *ab initio* scattering calculations extract such values as state-selected cross sections, angular distributions and time delays, errors in the calculated surfaces compound the problem of getting experimental verification of the scattering calculations. And since scattering calculations are based upon energy values extracted from an interpolating function fit to the calculated surface, it is desired that the error in the interpolating function be as small as possible when compared to the original calculated PES. Thus, from a scattering standpoint, the availability of both accurate PES's and reliable fits to those PES's are very important.

A number of fits to the calculated points will be presented along with some discussion of how well the global fitting functions represent these points.

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RC06 15 min 10:13

AB INITIO DIPOLE MOMENT SURFACE OF H₂O, G.S. KEDZIORA AND I. SHAVITT

The dipole moment surface and energy surface of H₂O was calculated using a high-quality basis set with 132 basis functions and a multi-reference CISD wavefunction with a 6-orbital complete-active-space reference. 312 points were calculated with energies up to 25000 cm⁻¹ above the minimum, including bond lengths from 0.770Å to 1.48Å and bond angles from 41° to 169°. The dipole moment surface will be compared with experiment and recent *ab initio* calculations. In addition, force constants and spectroscopic data from a perturbational treatment will also be presented.

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INTERMISSION

RC07 15 min 10:50

**MRSD-CI STUDIES OF THE LOW LYING ²Δ, ²Σ AND ²Π STATES OF TiN AND VC.
Saba M. Mattar**

The lowest ²Δ, ²Σ⁺ and ²Π states of VC are investigated using *ab initio* multireference single and double excitation configuration interaction (MRSD-CI). The dominant electronic configuration for the X²Δ ground state, the A²Σ⁺ and A'²Π states are 8σ² 3π_x² 3π_y² 1δ_{xy}⁺, 9σ⁺ 3π_x² 3π_y² and 9σ² 3π_x² 3π_y⁺ respectively. The A²Σ⁺←X²Δ transition is predicted to occur around 9056 cm⁻¹ while the A'²Π←X²Δ is estimated to lie around 16000 cm⁻¹. The spectroscopic parameters, R_e, ω_e, ω_eX_e, B_e, α_e, μ_e, dμ/dr|_e and the hyperfine coupling constants (b, b_F and c) are also computed for these three states. These are compared with the preliminary experimental results Morse *et al.* Similar extensive MRSD-CI calculations yield hyperfine coupling constants for isoelectronic TiN molecule that are in good agreement with the experimental results of Stiemle *et al.*

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RC08 15 min 11:07

ELECTRONIC STRUCTURE OF SiO: SPECTROSCOPY AND PHOTODISSOCIATION, I. Drira, N. Feautrier, A. Spielfiedel

The SiO molecule has been observed in circumstellar envelopes and in several sources, in particular in star-forming regions but not in cold clouds. Very recent studies suggest that the formation of this species must certainly be linked to high temperatures. This molecule has been localised in regions where the ultraviolet photons are abundant and it is necessary to know the photodissociation cross sections and reaction rates.

We report here *ab-initio* calculations of the energies of the first singlet excited states lying between the electronic ground state and the first dissociation asymptote. The atomic orbital basis set comprised 129 contracted functions including f functions on the two atoms.

First, we have calculated the MCSCF (Multiconfigurational Self Consistent Field) potential energy functions along the stretching coordinate ($C_{\infty v}$) for the singlet valence states ($X^1\Sigma^+$, $C^1\Sigma$, $D^1\Delta$, $A^1\Pi$) and the $E^1\Sigma^+$ which has some Rydberg character. All these states dissociate into (Si^3P+O^3P). As first pointed out by several authors¹, the latter $E^1\Sigma^+$ presents a barrier to dissociation resulting from interactions with higher $^1\Sigma^+$ states dissociating into (Si^1D+O^1D).

In the molecular region, the equilibrium distances R_e , the harmonic vibrational frequencies ω_e and the excitation energies T_e have been calculated in a large scale *ab-initio* Multireference Configuration interaction (MRCI) for the ground state and the first valence excited states ($C^1\Sigma$, $D^1\Delta$, $A^1\Pi$). In the MRCI calculations, all valence excitations from the reference wavefunction were included. These spectroscopic constants compare well with the experimental data².

For the first dipole allowed transition ($X^1\Sigma^+-A^1\Pi$), we have performed the calculation of the potential energy, electric dipole and transition moment functions of the two electronic states for values of the stretching coordinate ranging from the molecular to the dissociation region. To test the accuracy of these *ab initio* results, the calculated potential energies and electric dipole moments have been used in the evaluation of the vibration-rotation energy levels and the absorption spectrum at 300K which are in good agreement with the experimental spectrum².

The next step will be the determination of higher excited states which are important for dissociation studies.

¹ J.M. Robbe, J. Schamps, H. Lefebvre-Brion, and G. Raseev, J. Mol. Spect. **74**, 375 (1979)

² J. Hormes, M. Sauer, and R. Scullman, J. Mol. Spect. **98**, 1 (1983)

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RC09 15 min 11:24

A THEORETICAL STUDY OF THE SPECTROSCOPY AND DYNAMICS OF STACKED DIMERS OF AROMATIC HYDROCARBONS, R. G. SADYGOV, E. C. LIM

Energetics of the ground and excited singlet states of the stacked dimers of aromatic hydrocarbons have been investigated using INDO1/s method which incorporates the distance dependence of $\pi-\sigma$ interaction. The results provide the binding energy of the excimer fluorescence that are in satisfactory agreement with experiment. The results also account for the observed intervalence transitions from the lowest energy excimer state to a higher-lying excimer state which, in gas phase, leads to photofragmentation of the excimer.

Possible reasons for failure of phenanthrene to exhibit excimer fluorescence are also suggested by the computational results.

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RC10 10 min 11:41

ELECTRONIC STRUCTURE OF PROTACTINOCENE

Ke Zhao and Russell M. Pitzer

The electronic structure of protactinocene ($\text{Pa}(\text{C}_8\text{H}_8)_2$) was studied using *ab initio* quantum chemical methods including relativistic core potentials, gaussian double zeta basis sets, and spin-orbit configuration interaction calculations. The lower states of protactinocene are $5f^1$ states. The $5f_{+2}$ (e_{2u}) are raised in energy compared to the other $5f$ states¹ because of the interaction of the $5f_{+2}$ orbitals with the highest occupied ligand π MOs, while the $5f_{+3}$ (e_{3u}) states are lowered to a small extent by interaction with the unoccupied ligand π^* e_{3u} MOs. The $6d$ states are split apart much more due to their considerably stronger interactions¹ with ligand π orbitals, leaving only the $6d_0$ (a_{2u}) state at low energy. The ground state is thus $E_{5/2u}$ and transitions from it to the other $5f^1$ states and the low-lying $6d^1$ state are not allowed. The lowest allowed state was computed at 3.67 eV. The calculated ground state magnetic moment is 1.96 Bohr magnetons.

¹ A. H. H. Chang and R. M. Pitzer, J. Am. Chem. Soc., **111** (1989) 2500.

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RC11 10 min 11:53

AB INITIO CALCULATIONS FOR C_5S

S. Seeger, J. Flügge and P. Botschwina

C_5S was recently detected in the laboratory¹ and possibly also in the circumstellar envelope of IRC+10126². Making use of the CEPA-1³ method and a basis set of 184 contracted Gaussian-type orbitals we arrive at a linear equilibrium structure with the following bond lengths: $R_{1e} = 1.2855 \text{ \AA}$, $R_{2e} = 1.2924 \text{ \AA}$, $R_{3e} = 1.2707 \text{ \AA}$, $R_{4e} = 1.2800 \text{ \AA}$ and $R_{5e} = 1.5582 \text{ \AA}$ with the bonds ordered according to the chemical formula. The corresponding equilibrium rotational constant $B_e = 917.1 \text{ MHz}$ compares well with the experimental B_0 value¹ of 922.7 MHz. The equilibrium dipole moment calculated by CCSD(T)⁴ is as high as 5.38 D.

The wavenumbers and IR intensities of the stretching vibrations were determined using a well-established anharmonic model. The ν_1 band with origin at 2085 cm^{-1} was calculated to have a very large integrated IR intensity of 4000 km/mol . The ν_3 band at 1615.2 cm^{-1} is also very intense with $A_3 = 613 \text{ km/mol}$.

¹Y. Kasai, K. Obi, Y. Ohshima, Y. Hirahara, Y. Endo, K. Kawaguchi and A. Murakami, *Astrophys. J.* **L45**, 410 (1993)

²M. B. Bell, L. W. Avery and P. A. Feldman, *Astrophys. J.* **417**, L37 (1993)

³CEPA-1: Coupled Electron Pair Approximation, version 1; W. Meyer, *J. Chem. Phys.* **58**, 1017 (1973).

⁴Coupled Cluster method with single and double excitation operators and a quasiperturbative treatment of the effects of connected triple excitations; K. Raghavachari, G. W. Trucks, J. A. Pople and M. Head-Gordon, *Chem. Phys. Lett.* **157**, 479 (1989).

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RD01 15 min 8:30

Infrared Diode Laser Spectroscopy of the ν_3 Fundamental and $\nu_3 + \nu_5 - \nu_5$ Sequence Bands of the C_4 Radical in a Hollow Cathode Discharge, N. Moazzen-Ahmadi, J.J. Thong, and A.R.W. McKellar

The infrared absorption spectrum of the linear C_4 radical has been studied in an extension of the original observation of gas-phase C_4 by Heath and Saykally.¹ The experiment was performed using a flowing mixture of acetylene and helium subjected to hollow-cathode discharge, which was probed in the 1525-1570 cm^{-1} spectral region using a tunable diode laser spectrometer. Transitions with N-values up to 60 were measured. Their analysis yielded band origins, rotational and centrifugal distortion parameters for the lower and upper vibrational states, and l-type doubling parameters for the degenerate bending states $v_5=1$ and $(v_3=1, v_5=1)$. In particular, the ν_3 origin was determined to be 1548.6128(4) cm^{-1} , the ground state rotational and centrifugal distortion parameters were $B=4979.89(21)$ MHz and $D=0.848$ kHz, and the l-doubling parameter for $v_5=1$ was $q_5=10.98(13)$ MHz. This value for q_5 was used to estimate the ν_5 frequency of gas-phase C_4 to be $160 \pm 4 \text{ cm}^{-1}$. In addition, tentative identification of the sequence band $\nu_3 + \nu_4 - \nu_4$ has been made. Efforts are underway to measure more lines of this band to perform a complete analysis. The observations to date are consistent with a linear structure for the triplet ground state of C_4 , and show no effects of quasilinearity.

1. J.R. Heath and Saykally, J.Chem. Phys. **94**, 3271 (1991).

Address of N. Moazzen-Ahmadi and J.J. Thong: Department of Physics, University of Lethbridge, Lethbridge, Alberta T1K 3M4, Canada.

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RD02 10 min 8:47

THE HYPERFINE STRUCTURE OF CuCl IN ITS GROUND AND EXCITED VIBRATIONAL STATES STUDIED BY MICROWAVE FOURIER TRANSFORM (MWFT) SPECTROSCOPY, R.J. LOW, T.D. VARBERG, J.P. CONNELLY, A.R. AUTY, B.J. HOWARD AND J.M. BROWN

Metal compounds are of particular interest as they provide tests of simple models of transition metal bonding^{1,2}. We have measured the hyperfine structure of the $J=1 \leftarrow 0$ rotational transition of CuCl in the $v=0, 1$ and 2 vibrational states using the technique of MWFT spectroscopy. The molecules were produced in the gas phase by laser ablation of a solid sample of CuCl . The ablation took place just in front of the supersonic expansion nozzle which had the effect of rotationally cooling the molecules, while leaving them vibrationally excited. The analysis of the hyperfine structure yielded improved values of the rotational and electric quadrupole constants as well as determining for the first time the nuclear spin-rotation constants^{3,4}. The vibrational dependence of these major parameters along with the physical implication will be discussed.

¹ R.J. Low, T.D. Varberg, J.P. Connelly, A.R. Auty, B.J. Howard and J.M. Brown, J. Mol. Spec. **161**, 499 (1993).

² K.D. Hensel, C. Styger, W. Jäger, A.J. Merer and M.C.L. Gerry, J. Chem. Phys. **99**, 3320 (1993).

³ E. Tiemann and J. Hoefft, Z. Naturforsch. **32a**, 1477 (1977).

⁴ E.L. Manson, F.C. De Lucia and W. Gordy, J. Chem. Phys. **62**, 1040 (1975).

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RD03 10 min 8:59

UV SPECTROSCOPY OF THE B²A' AND C²A'' STATES OF FCO. M. Matti Maricq and Joseph J. Szente, Yi Su and Joseph S. Francisco

Gas phase UV spectra of FC¹⁶O and FC¹⁸O, produced by laser photolysis of F₂ in the presence of CO, are obtained in the region between 29000 cm⁻¹ and 43000 cm⁻¹(1). The three prominent progressions are assigned to the B²A' and C²A'' states of FCO and a fourth, weaker progression may belong to the second excited ²A' state. For the B²A' state, we obtained vibrational frequencies of $\nu_1 = 1120 \pm 40$ cm⁻¹ and $\nu_2 = 780 \pm 30$ cm⁻¹ and a zero point energy in the range 24000 < T₀ < 27000 cm⁻¹. The spectrum of the C²A'' state yields $\nu_1 = 1458 \pm 6$ cm⁻¹ and $\nu_2 = 651 \pm 2$ cm⁻¹ and a zero point energy of T₀ = 28500 ± 25 cm⁻¹. The electronic energies and vibrational frequencies are compared to recent *ab initio* calculations.

(1). M. M. Maricq and J. J. Szente, Yi Su and J. S. Francisco, J. Chem. Phys. submitted.

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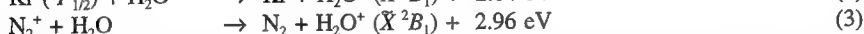
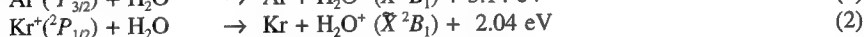
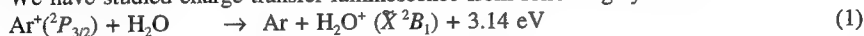
RD04 15 min 9:11

**X⁺ (X=Ar, Kr, N₂) + H₂O charge-transfer luminescence:
Vibrationally-selected H₂O⁺ \tilde{A} - \tilde{X} emissions**

Rainer A. Dressler, Susan T. Arnold, James A. Gardner,^a and Edmond Murad
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Exothermic low-energy (1-20 eV, c.m.) charge-transfer reactions are primarily governed by the energy resonance criterion. They thus offer a convenient means of producing ions in a narrow energy range of rovibronic states. A further constraint on the probability of populating near-resonant charge-transfer states is the necessity of a favorable Franck-Condon overlap between the vibrational wavefunctions of the reactants and the products. Rotational energy transfer is insignificant due to the long-range nature of charge-transfer processes. Consequently, if electronically excited states are accessed in near-resonant charge-transfer collisions, emission spectra can be observed involving only few excited state vibrational levels with near-thermal rotational distributions.

We have studied charge-transfer luminescence from following systems:



The luminescence is produced by propagating a mass and energy-selected ion beam through a collision cell that is fiber-optically coupled to an optical multichannel analyzer. The 0.5 nm (fwhm) resolution spectra show that the reaction exothermicity is almost exclusively partitioned to internal modes of H₂O⁺, yielding H₂O⁺ \tilde{A} ₁ state products in few bending vibrational levels at energies given by the respective exothermicities. In some cases emissions from previously not observed high *K* levels (up to *K* = 6) are identified that are related to dynamical effects. The most recent Kr⁺ + H₂O luminescence measurements are carried out with a very sensitive liquid-nitrogen cooled CCD detector providing greater than 40% quantum efficiency in the 600-800 nm range. We plan measurements at considerably higher resolution and hope to determine hitherto unknown spectroscopic constants in order to support the numerous computational studies of the H₂O⁺ \tilde{A} ₁- \tilde{X} ²B₁ Renner-Teller system.

RD05 15 min 9:28

VIBRATIONAL PREDISSOCIATION SPECTROSCOPY OF PROTONATED MOLECULES

YIBIN CAO, JONG-HO CHOI, BERND-MICHAEL HAAS, AND MITCHIO OKUMURA

Protonated chlorine nitrate and protonated nitric acid have been proposed as important reactive intermediates in stratospheric chemistry. We report infrared spectra which reveal that both of these species can exist in two isomeric forms, depending on the site of protonation, consistent with *ab initio* studies by Lee and Rice. The most stable isomers are weakly bound complexes, $\text{NO}_2^+(\text{H}_2\text{O})$ and $\text{NO}_2^+(\text{HOCl})$, formed by protonation of the OH (ClO) group. These clusters readily predissociate upon absorption of one or two photons pumping the OH stretch bands. Protonation of a terminal O atom form higher energy covalently-bound species which must isomerize by a photon-induced intramolecular proton transfer in order to dissociate. These isomers can be distinguished by their infrared spectra and the conditions for their formation. Anomalous intensities in the IR spectrum of a related ionospheric species, protonated nitrous acid, suggest that dynamical effects (IVR or dissociation rates) may be important in determining intensities observed in two-photon predissociation spectra.

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RD06 15 min 9:45

INFRARED SPECTROSCOPIC STUDIES OF $\text{NO}^+(\text{H}_2\text{O})_n$ CLUSTERS, $n=1-5$

JONG-HO CHOI, KEITH T. KUWATA, BERND-MICHAEL HAAS, YIBIN CAO, MATTHEW S. JOHNSON, and MITCHIO OKUMURA

Studies of solvated cluster ions can provide insights into the microscopic aspects of solvent-induced intracluster reactions. We have obtained infrared spectra of mass-selected $\text{NO}^+(\text{H}_2\text{O})_n$ cluster ions for $n=1-5$ in the 2700-3800 cm^{-1} region by vibrational predissociation spectroscopy. On the basis of the observed photodissociation behavior and infrared spectra, qualitative structural information about $\text{NO}^+(\text{H}_2\text{O})_n$ was derived. In the smaller clusters, the spectra indicate that H_2O ligands are bound to a nitrosonium ion core, but there is a dramatic change in the infrared spectrum at $n=5$, indicating that upon sufficient hydration an intracluster reaction occurs: $\text{NO}^+(\text{H}_2\text{O})_4 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+(\text{H}_2\text{O})_3(\text{HONO})$. In the larger clusters, hydrogen-bonding stabilization strongly favors formation of the hydronium ion core, H_3O^+ . We have also performed *ab initio* calculations to estimate vibrational frequencies and binding for $n=1$ and $n=2$ in order to aid in interpreting the observed spectra and photodissociation processes.

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INTERMISSION

RD07 15 min 10:20

GAS PHASE SOLVATION OF Na^+ with CH_3NH_2 : Spectroscopic and Computational Results

ORLANDO M. CABARCOS, THOMAS J. SELEGUE, AND JAMES M. LISY

Vibrational predissociation spectra have been recorded for $\text{Na}^+(\text{CH}_3\text{NH}_2)_n$, $n = 5-20$ in the P-branch of the 9.6μ region of the CO_2 laser ($1016-1056 \text{ cm}^{-1}$). No other predissociation was observed in any other portion of the CO_2 spectral range.

At $n = 10$ there is an abrupt 4 cm^{-1} blue shift in absorption to 1038 cm^{-1} . This is indicative of a structural change in the ion cluster. At $n = 12$ the peak shifts a second time to 1039 cm^{-1} . There is no further change in absorption frequency seen for the remaining cluster sizes up to $n=20$.

Monte Carlo (MC) and Molecular Dynamics (MD) simulations have been employed to help elucidate the nature of the structural changes. MC and MD results have been obtained for $\text{Na}^+(\text{CH}_3\text{NH}_2)_n$; $n = 6-12$ at various temperatures. Both methods indicate that for $n = 6-8$, the dominant configuration consists of 5 solvents in the first solvation shell. At $n \geq 9$, a new configuration appears which places 6 molecules in the first solvation shell.

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RD08 15 min 10:37

THE VIBRATIONAL STARK EFFECT AND $\text{Cs}^+(\text{NH}_3)_n$ AND $\text{Cs}^+(\text{CH}_3\text{OH})_m$ ION CLUSTERS

ORLANDO M. CABARCOS AND JAMES M. LISY

The vibrational Stark effect¹ has been used to calculate the frequency shifts observed in the vibrational predissociation spectra of $\text{Cs}^+(\text{NH}_3)_n$; $n=5-12$, and $\text{Cs}^+(\text{CH}_3\text{OH})_m$; $m=5-12$, ion clusters. The electric field was obtained for each cluster by averaging over 400 Monte Carlo generated configurations. The ligands were approximated by polarizable dipoles and the ion was treated as a point charge.

Experimental results will be compared to calculated frequency shifts and ligand effects will also be discussed.

¹D. M. Bishop, J. Chem. Phys. **98** (4), 3179 1992

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RD09 15 min 10:54

ANGULAR MOMENTUM COUPLING IN $AX(^2\Pi)$ -Rg COMPLEXES, W. H. BASINGER, U. SCHNUPF, AND
M. C. HEAVEN

The details of angular momentum coupling in $AX(^2\Pi)$ -Rg complexes are dependent on several factors. These include the strength of spin-orbit coupling in the monomer and the relative anisotropies of the average and difference potential energy surfaces. To date, attention has been focused on systems where a Hund's case (a) monomer is bound to a rare gas atom^{1,2} (in particular, $OH(X^2\Pi)$ -Ar). For this situation the rotational energy levels of the complex are generally characterized by half-integer quantum numbers. However, in examining models for $AX(^2\Pi)$ -Rg complexes we found that rotational levels characterized by integer rotational quantum numbers (case (b)-like behavior) can be observed under a variety of circumstances. Of particular interest is the fact that integer quantum numbers do not necessarily imply that quenching of the orbital electronic angular momentum has occurred. We have also found that, for near-symmetric average potentials, the difference potential can play an important role in determining the angular momentum coupling scheme. These principles will be illustrated with examples drawn from studies of $CH/D(X^2\Pi)$ -Rg (Rg=Ne, Ar) and $CN(A^2\Pi)$ -Ne.

1. M.-L. Dubernet, D. Flower, and J. M. Hutson, *J. Chem. Phys.* **94**, 7602 (1991)
2. W. H. Green and M. I. Lester, *J. Chem. Phys.* **96**, 2573 (1992)

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RD10 15 min 11:11

**Vibrational Analysis of the $\tilde{A} \leftarrow \tilde{X}$ Transition of
Rg•SH Complexes (Rg = Ne, Ar and Kr)**

Min-Chieh Yang, Aldo P. Salzberg, Christopher C. Carter, and
Terry A. Miller

The LIF spectra of Rg•SH complexes have been observed. Vibrational analysis of these spectra indicates that in Ne•SH, most of observed bands are transitions to the internal rotational levels of the \tilde{A} state. In Ar•SH and Kr•SH, we observed both pure van der Waals stretch bands and bend-stretch combination bands. Based on the isotopic shift between $Kr^{86}\bullet SH$ and $Kr^{84}\bullet SH$, we are able to determine the absolute vibrational assignment of most observed Kr•SH bands. The details of analysis will be presented.

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RD11 15 min 11:28**HIGH RESOLUTION, ELECTRONIC SPECTROSCOPY OF THE RARE GAS (Ne, Ar, Kr) •SH/D VAN DER WAALS COMPLEXES**CHRISTOPHER C. CARTER, JAMES M. WILLIAMSON, AND TERRY A. MILLER

The rotationally resolved, jet-cooled, electronic spectra of the SH/D rare gas complexes, Rg•SH/D (Rg = Ne, Ar, Kr) have been recorded. The complexes were produced by the UV photolysis of small percentage mixtures of either H₂S or D₂S in He with the appropriate rare gas and then probed via LIF with a pulse amplified cw ring dye laser. We were able to resolve (≈ 300 MHz laser linewidth) both fine and hyperfine components of these complexes. Data for both pure van der Waals stretch bands as well as bend-stretch combination bands have been recorded for each complex. The analysis of these spectra will be presented and discussed.

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RD12 15 min 11:45**HIGH RESOLUTION, ELECTRONIC SPECTROSCOPY OF RARE GAS •OH/D AND •SH/D COMPLEXES**CHRISTOPHER C. CARTER, BOR-CHEN CHANG, JAMES M. WILLIAMSON, AND TERRY A. MILLER

We have recorded and analyzed the rotationally resolved, laser-induced fluorescence spectra of the rare gas (Rg), Rg•OH/D and the analogous Rg•SH/D complexes (Rg = Ne, Ar, Kr). The rotational, fine and hyperfine structure is observed for all these complexes in transitions involving solely the van der Waals stretch as well as transitions involving bend-stretch combinations.

We have recently obtained high resolution spectra (≈ 300 MHz) of the Kr•OH/D complex. These new results will be presented along with a full overview of the Rg•OH/D and Rg•SH/D data that has been taken in our laboratory.

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RD13

15 min

12:02

Electronic Spectroscopy and Dynamics of the CH/D-Ne Van der Waals Complexes.
W. H. Basinger, U. Schnupf, and M.C. Heaven

Rotationally resolved spectra for the $A^2\Delta-X^2\Pi$ and $B^2\Sigma-X^2\Pi$ transitions of $CH/D-Ne^1$ have been recorded. Bands of both the A-X and B-X complexes were observed in association with the monomer 0-0 transition. In addition, complex bands associated with the B-X monomer 1-0 transition were also recorded. Analyses of the ro-vibronic structures show that the complex is weakly bound in both the ground (X) and excited (A,B) electronic states. Preliminary results from the analysis of the highly congested A-X bands indicate that intermolecular bond length is unchanged upon excitation. A more detailed analysis is in progress and will be addressed. Analysis of the bands in the B-X system indicate that excitation to the B state reduces the binding energy and lengthens the intermolecular bond. The rotational levels of the X state were characterized by half-integer quantum numbers. This is in contrast to the situation for $CH(X)-Ar^2$ where the ground state exhibits integer rotational quantum numbers. The $n=2$ and $n=1, k=0$ bands in the B-X system showed homogeneous line broadening as a result of rotational predissociation of the CH-Ne complex. B-X complex band assignments, rotational constants, and predissociation lifetimes will be discussed.

Calculations are currently in progress on the A-X system of CH/D-Ne in order to elucidate the origins of the rich rotational contours observed. Details and progress of the calculation will be reported on.

1) W. H. Basinger, U. Schnupf, and M. C. Heaven, *Electronic Spectroscopy and Dynamics of the CH/D-Ne Van der Waals Complex*. Submitted to: Faraday Discussion No. 97. Structure and Dynamics of Van der Waals Complexes.

2) G. W. Lemire, M. J. McQuaid, A. J. Kotlar, and R. C. Sausa, *J. Chem. Phys.*, 1993, 99, 91

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RE01 15 min 1:30**MICROWAVE - MILLIMETER-WAVE DOUBLE RESONANCE EXPERIMENTS ON Ar-CO**Wolfgang Jäger and Michael C.L. Gerry

A double resonance technique has been developed to extend the accessible range of cavity microwave Fourier transform spectrometers to millimeter-wave frequencies. The method uses a modulation scheme with pulsed microwave and continuous millimeter-wave radiation.

This technique has been applied to measure the frequencies of low J *b*-type rotational transitions of the van der Waals dimer Ar-CO in the frequency range 70-90 GHz. This complements previous studies in the infrared¹ and microwave² regions which have shown that Ar-CO is a T-shaped complex undergoing large amplitude motions. The present work has resulted in a precise value for the A-rotational constant, initially obtained in the infrared work from combination differences.

The experimental technique will be discussed and the results will be interpreted in terms of structural and dynamical parameters of the complex.

¹ A.R.W. McKellar, Y.P. Zeng, S.W. Sharpe, C. Wittig, and R.A. Beaudet, *J. Mol. Spectrosc.* **153**, 475 (1992).

² T. Ogata, W. Jäger, I. Ozier, and M.C.L. Gerry, *J. Chem. Phys.* **98**, 9399 (1993).

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RE02 15 min 1:47**Pure Rotational Spectra of the van der Waals Dimer Xe-CO**Kaley A. Walker, Wolfgang Jäger and Michael C.L. Gerry

Pure rotational spectra of 17 isotopic species of the van der Waals dimer Xe-CO have been measured with a cavity microwave Fourier transform spectrometer in the frequency region 4.5 - 15 GHz. This dimer has previously been observed in the infrared region¹. The Xe-CO complex is a near prolate asymmetric rotor. The observed transitions are *a*-type R-branches, having $\Delta J = +1$ and $\Delta K_a = 0$ for levels with $K_a = 0$. The derived constants are used to determine an effective structure and to approximate the van der Waals stretching frequency. Comparisons will be made with the properties of other rare gas-carbon monoxide dimers.

¹ J.W.C. Johns, Z. Lu, and A.R.W. McKellar, *J. Mol. Spectrosc.* **159**, 210 (1992).

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RE03 15 min 2:04
INFRARED SPECTRA AND ANISOTROPIC POTENTIAL ENERGY SURFACES FOR He-CO and H₂-CO

 Claudio E. Chuaqui, Robert J. Le Roy and A. Robert W. McKellar

For both the ³He-CO and ⁴He-CO, and the H₂-CO and D₂-CO Van der Waals dimers, fully resolved infrared spectra have been measured in the 4.7 μm region near the fundamental band origin of the CO monomer. Only a small fraction of the observed lines could be assigned using conventional spectroscopic techniques, and little insight was gained from synthetic spectra generated from published *ab initio* potentials for these systems. However, comparisons with synthetic spectra generated from various other trial potentials led to complete sets of assignments for the He complexes and near-complete sets for the H₂(j=0)-CO and D₂(j=0)-CO species. These in turn allowed us to determine new anisotropic potential energy surfaces for these species which differ markedly with those reported, previously and raise interesting questions regarding the tests of previous potential surfaces based on very low temperature microwave line broadening cross sections.

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RE04 15 min 2:21
MODEL POTENTIAL FUNCTIONS FOR VAN DER WAALS TRIMERS CONTAINING CARBON DIOXIDE AND ACETYLENE
Zhenlan Li and J. S. Muentert

There are four different trimeric van der Waals complexes containing carbon dioxide and acetylene: (CO₂)₃, (HCCH)₃, (CO₂)₂HCCH, and (HCCH)₂CO₂. Infrared spectra of (CO₂)₃ and (HCCH)₃ have been studied and these molecules exhibit planar structures having three fold symmetry axes. The two mixed trimers have not been observed. Potential functions for this series of complexes have been constructed using a model containing repulsion, dispersion, and electrostatic interactions. Each of these terms are distributed among the atoms of the individual molecules. No adjustable parameters are used in the potential functions discussed here. The results for acetylene trimer are in excellent agreement with experiment. The CO₂ trimer potential contains two stable configurations: one in agreement with the experimental structure, and a second nonplanar configuration. Two different high barrier inversion paths, that permit internal rotation of the monomers within the complex, are found in both (HCCH)₃ and (CO₂)₃. Numerous local minima are observed in the potential functions for both (CO₂)₂HCCH and (HCCH)₂CO₂. These configurations represent both planar and nonplanar geometries. These results suggest that the absence of experimental data for the mixed trimers arises in part from the effects of large amplitude motions sampling multiple configurations. All of the local minimum structures can be understood by considering the trimers as sums of dimeric species.

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RE05 15 min 2:38

OBSERVATION OF THE LOWEST BENDING STATE OF HEHCN BY MOLECULAR BEAM ELECTRIC RESONANCE, S. DRUCKER, F.-M. TAO, AND W. KLEMPERER

The lowest bending state of HeHCN has been observed by mm-wave electric resonance optothermal spectroscopy.¹ Transitions originating in the ground vibrational state were recorded at 101.4 GHz and 105.8 GHz. Pure rotational transitions were observed at 15.9 GHz and 31.1 GHz in double resonance with the 101.4 GHz line. The bending state correlates to $j_{\text{HCN}} = 1$ in the limit of free internal rotation. Fine structure in the spectrum arises from the rotation of the pseudodiatom complex comprised of He and HCN subunits. Coupling to the HCN rotation splits these levels and prevents a spectral pattern with simple dependence on the total angular momentum J . To aid the J assignment, we have computed rovibrational energies and wavefunctions arising from an *ab initio* intermolecular potential, calculated at the MP4 level using a very large basis set containing bond functions.² Calculated and observed transition frequencies, including hyperfine structure, agree to within 10%. This comparison, used in conjunction with calculated transition intensities, establishes rotational assignments for the observed lines. The 15.9 GHz line is assigned as the ground state $J = 1 \leftarrow 0$ transition. Its observation requires double resonance with the 101.4 GHz line, suggesting that only the vibrationally excited molecules strike the detector. This implies a nearly free internal rotor description of the ground state, in which the vibrationally averaged dipole moment is too small to produce the required deflection in the electrostatic hexapole focuser. Resolved hyperfine structure in the 101.4 GHz transition also indicates large angular excursion of the HCN in the ground state of this complex. The ground state value of $eq_{aa}Q$ is $-0.567(60)$ MHz, giving $\langle P_2(\cos \theta) \rangle = 0.120$. This value is very close to $\langle P_2(\cos \theta) \rangle = 0$, characteristic of a $j = 0$ free internal rotor.

1. G.T. Fraser, R.D. Suenram, and L.H. Coudert, *J. Chem. Phys.* **90**, 6077 (1989).
2. F.-M. Tao, *J. Chem. Phys.* **98**, 3049 (1993).

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RE06 15 min 2:55

AB INITIO POTENTIALS AND DYNAMICS FOR HE-CO, AR-HCCH, AND AR-HCN, FU-MING TAO, S. DRUCKER, R. COHEN, AND W. KLEMPERER

We present *ab initio* potential surfaces and rovibrational levels for He-CO, Ar-HCCH, and Ar-HCN. The intermolecular potentials are calculated using Møller-Plesset perturbation theory up to the complete fourth-order (MP4) and efficient basis sets containing bond functions. The rovibrational energies and spectroscopic constants are calculated using the collocation method with the potential values at the collocation points given by spline interpolation or by an analytical fit to the *ab initio* values. For He-CO, the potential surface is consistent with the $V_{3,3,3}$ potential of Chuaqui and Le Roy,¹ but differs significantly from the latest empirical (XC) potential of Le Roy *et al.*² and an earlier *ab initio* calculation.³ The energy levels predicted from our potential are compared with experiment. For Ar-HCCH, our potential shows a very flat minimum region from $\theta = 70^\circ$ to 110° (energy change $\leq 1.0 \text{ cm}^{-1}$), in contrast to a high barrier (25 cm^{-1}) of the recent empirical potential by Bemish *et al.*⁴ The energy levels and spectroscopic constants predicted from our potential are compared with experiment. For Ar-HCN, we explicitly considered the effect of HCN bending vibration on the global potential and particularly on the potential anisotropy. The energy levels and spectroscopic constants arising from the calculated potential are compared with experiment.

1. C.E. Chuaqui, R.J. Le Roy, and A.R.W. McKellar, *J. Chem. Phys.*, submitted.
2. R.J. Le Roy, C. Bissonnette, T.H. Wu, A.K. Dham, and W.J. Meath, *Faraday Discussion* No. 97 (1994).
3. L.D. Thomas, W.P. Kraemer, and G.H.F. Dierksen, *J. Chem. Phys.* **51**, 131 (1980).
4. R.J. Bemish, P.A. Block, L.G. Pedersen, W. Yang, and R.E. Miller, *J. Chem. Phys.* **99**, 8585 (1993).

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RE07 15 min 3:12

THE POTENTIAL ENERGY SURFACE OF $\text{Ne-C}_2\text{H}_2$ FROM INFRARED SPECTROSCOPY AND THEORY, R.J. Bemish And R.E. Miller

Infrared spectra have been obtained for the $\text{Ne-C}_2\text{H}_2$ complex using the optothermal detection method. The spectrum bears little resemblance to that of a rigid molecule, but rather shows clumps of transitions near the monomer transition frequencies. The implication is that the acetylene sub-unit undergoes nearly free rotation within the complex. To assign this spectrum, we have made use of the collocation method, in combination with an HFD potential, initially arrived at from a combination of *ab initio* calculations and by scaling the parameters obtained previously from the $\text{Ar-C}_2\text{H}_2$ complex. The collocation method allows us to calculate both the energy levels and the associated wavefunctions for a trial potential, from which the spectrum of the complex can also be calculated. This trial potential was then modified to fit the experimental spectrum. When combined with the previous study of the $\text{Ar-C}_2\text{H}_2$ complex, these results provide new insights into the way in which the long range dispersion interactions need to be handled in molecules that are spatially extended.

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INTERMISSION

RE08 15 min 3:45

THE SPECTROSCOPY AND INTERNAL TUNNELING DYNAMICS OF THE $\text{C}_2\text{H}_4\text{-CO}_2$ AND $\text{C}_2\text{H}_4\text{-N}_2\text{O}$ COMPLEXES: TWO DISTINCTLY DIFFERENT SYSTEMS; P.A. Block, Won Rhee and R.E. Miller.

We report the first infrared spectra of the ethylene-carbon dioxide and ethylene-nitrous oxide complexes. These rotationally resolved spectra provide detailed information on the equilibrium structures for these complexes, as well as information on the potential energy surface along the coordinate corresponding to the internal rotation of the two molecules relative to one another. In both cases, the rotational constants are consistent with a stacked structure, in which the long axis of the molecules are parallel. The surprising result is that the spectrum of ethylene-carbon dioxide shows sub-bands that are strongly shifted from the expected rigid rotor origins, characteristic of internal rotation, while no such shifts are observed for the ethylene-nitrous oxide case. The differences between these two systems are explained with the aid of *ab initio* calculations of the potential energy surface along the internal rotation coordinate. The rather unique pattern observed for the sub-band origin shifts in the ethylene-carbon dioxide spectrum results from an extremely low barrier to internal rotation and the coincidental relative sizes of the rotational constants of the carbon dioxide and ethylene monomer units.

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RE09

15 min

4:02

VIBRATIONAL EIGENSTATE DETERMINATIONS:
IMPROVEMENTS TO THE COLLOCATION METHOD

P. KORAMBATH P. PENDERGAST Z. DARAKJIAN AND E. F. HAYES

The collocation method [1] is often used to obtain accurate eigenvalues for polyatomic bound-state problems. The basis of this method is a fitting scheme wherein the wave function is taken to be exact at a preselected set of points, namely the collocation points. The imposition of this condition ultimately leads to a generalized eigenvalue problem. The purpose of this paper is to report recent progress in enhancing the accuracy and speed of the diagonalization phase of the collocation method through the use of the Implicitly Restarted Lanczos Method (IRLM) of Sorensen [2].

For the generalized eigenvalue problem, the shift-and-invert version of the IRLM is used in conjunction with various local-support basis sets designed to achieve optimal sparsity of the Hamiltonian. This allows one to use sparse matrix technology to obtain the eigenvalues and eigenvectors of interest.

Applications of the method to van der Waals complexes such as $\text{Ar-C}_2\text{H}_2$ will be reported.

1. Peet, A. C. and Yang, W., J. Chem. Phys. **90**, 1746 (1989).
2. Sorensen, D. C. "The k-step Arnoldi Process". In Large-scale Numerical Optimization, T. F. Coleman and Yuying Li eds. SIAM Publications, Philadelphia, PA, 228-237.

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RE10

15 min

4:19

VIBRATIONAL COUPLINGS AND ENERGY FLOW IN COMPLEXES OF $\text{HC}\equiv\text{CH}$, $\text{HC}\equiv\text{CD}$, $\text{HC}\equiv\text{CC}\equiv\text{CH}$,
and $\text{N}\equiv\text{CH}$ WITH NH_3

G. Hilpert, G.T. Fraser, and A.S. Pine

Infrared spectra of the C-H stretching vibrations of the symmetric-top complexes, $\text{HC}\equiv\text{CH--NH}_3$, $\text{HC}\equiv\text{CD--NH}_3$, $\text{HC}\equiv\text{CC}\equiv\text{CH--NH}_3$, and $\text{N}\equiv\text{CH--NH}_3$, have been recorded using a color-center-laser electric-resonance optothermal spectrometer. Efforts to observe the N-H stretches were unsuccessful. The hydrogen-bonded C-H stretching modes of $\text{HC}\equiv\text{CH--NH}_3$ and $\text{N}\equiv\text{CH--NH}_3$ are strongly coupled to the hydrogen bond as evidenced by their large monomer red-shifts of 75 and 200 cm^{-1} and broad predissociation linewidths of 2000 and 650-800 MHz, respectively. The complexation-induced asymmetry in $\text{HC}\equiv\text{CH--NH}_3$ is not sufficient to allow us to observe the local mode associated with the outer C-H stretch. However, isotopic substitution in $\text{HC}\equiv\text{CD--NH}_3$ shows that this mode is red shifted by less than 1 cm^{-1} from the monomer vibration. The narrow predissociation linewidths of this mode (7 - 12 MHz) are consistent with this small red shift. The weaker coupling of the C-H stretches in $\text{HC}\equiv\text{CC}\equiv\text{CH}$ is completely quenched upon complexation with NH_3 . The outer C-H stretch is observed in the diacetylene ($\text{HC}\equiv\text{CC}\equiv\text{CH}$) complex, blue shifted by approximately 0.3 cm^{-1} from the infrared-active monomer C-H stretch at 3333.7 cm^{-1} ; the bound CH stretch is red shifted about the same amount as in $\text{HC}\equiv\text{CH--NH}_3$. These observations imply that the weak coupling of the local modes in diacetylene is significantly quenched upon complexation with NH_3 . The $\text{HC}\equiv\text{CC}\equiv\text{CH--NH}_3$ predissociation linewidths are similar to those in $\text{HC}\equiv\text{CD--NH}_3$, even though the outer C-H stretch is now five bonds away from the hydrogen bond. Surprisingly, these results suggest that the length of the triple-bond backbone in acetylene chains does not significantly impede the rate of vibrational energy flow. Future efforts will be made to extend these studies to the triacetylene complex, $\text{HC}\equiv\text{CC}\equiv\text{CC}\equiv\text{CH--NH}_3$.

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RE11 15 min 4:36

THE SPECTROSCOPY AND DYNAMICS OF THE HF-DF and DF-HF DIMERS:
DISSOCIATION ENERGIES AND FINAL STATE DISTRIBUTIONS, R.J. Bemish, Ming
Wu, E.J. Bohac and R.E. Miller.

Infrared spectra have been recorded for both isomers of the HF-DF dimer, namely where either the HF or the DF act as the proton donor. For the case of HF-DF we have observed both the $K_a=0\leftarrow 0$ and the $K_a=1\leftarrow 0$ sub-bands associated with the HF stretch. For the DF-HF isomer only the $K_a=0\leftarrow 0$ sub-band is observed since the proton donor lies very nearly along the A-axis of the complex. Photofragment angular distributions have also been recorded for all three sub-bands, yielding information on the final rotational state distributions. The results agree with the earlier work on HF dimer¹, which showed with the proton donor molecule is highly rotationally excited while the acceptor molecule is preferentially produced in low j states. Dissociation energies are also reported for both of the isomers and compared with the results of recent theoretical calculations².

1. E. J. Bohac, M. D. Marshall, R. E. Miller, *J. Chem. Phys.* 96, 6681 (1992).

2. M. Quack, M. A. Suhm, *J. Chem. Phys.* 95, 28 (1991).

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RE12 15 min 4:53

PHOTODISSOCIATION OF ORIENTED MOLECULES: APPLICATION TO THE N₂-HF
COMPLEX, R.J. Bemish and R.E. Miller.

Due to their highly non-statistical behavior, weakly bound complexes provide us with an interesting class of molecules for studying unimolecular dissociation. We have developed a number of new methods for studying the photodissociation of these species resulting from infrared excitation. Recently we have made use of large DC electric fields to orient the parent complex prior to dissociation. This talk will outline the influence this initial orientation has on the photofragment angular distributions measured using a rotatable optothermal instrument. A number of systems will be discussed, with the emphasis being on the N₂-HF complex for which we now have a complete assignment of the final rotational/vibrational/translational state distributions of both fragments, along with the intermolecular scalar correlations. Conservation of energy is then used to determine the dissociation energy of the complex.

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RE13 15 min 5:10

LASER-INDUCED-FLUORESCENCE DETECTION OF OVERTONE TRANSITIONS OF TWO HF CONTAINING COMPLEXES, S. TSANG, H. CHANG, R. MOLLAAGHABABA AND W. KLEMPERER

The high-resolution laser-induced fluorescence spectra of the $v = 3$ excitation of the HF stretch in HFHCl and N_2HF molecules are measured. The complexes are formed in a super-sonic jet with HFHCl in an argon expansion and N_2HF in a nitrogen expansion. For HFHCl , a single band with $K = 0$, $\Delta K = 0$ of both isotopic species, was observed; and for N_2HF , both the $\Sigma - \Sigma$ second overtone of pure HF stretch and the $\Pi - \Pi$ hot band of the N_2 bend were recorded. The HF submolecule was pumped from $v = 0$ to $v = 3$ by radiation from a Ti:Sapphire ring laser operating in the 800 – 900 nm range. Both $\Delta v = 1$ and $\Delta v = 2$ emission of the HF fragment were observed by large area PbS and Ge detectors, respectively. The average linewidth of 300 MHz in this overtone region is approximately 30 times greater than at the fundamental. The linewidths of the vibration-rotation transitions of HFHCl show considerable variations with both Cl isotope and J level. Although the isotopic dependence of the linewidths was observed in the fundamental, no perceptible J-dependence was detected. The observed rotational temperature of N_2HF , 17 K, is higher than the typical rotational temperatures observed for complexes produced in argon expansion of 11 K.

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RE14 15 min 5:27

THE BRANCHING RATIOS OF $V = 2$ AND $V = 1$ CHANNELS OF HF_2 and HFHCl AFTER PHOTO-DISSOCIATION, R. MOLLAAGHABABA, H. CHANG, D. D. NELSON AND W. KLEMPERER

We present the branching ratios for $v = 2$ and $v = 1$ levels of the HF fragment after photo-dissociation of $N = v_1 + v_2 = 3$ bands of $(\text{HF})_2$ and $v = 3$ HF stretch of HFHCl . The molecular complexes are produced in super-sonic jets which are intracavity in a Ti:Sapphire ring laser to exploit the high power necessary for pumping weak overtone transitions. The HF submolecule at $v = 3$ has vibrational excitation which is 10^4 cm^{-1} in excess of the binding energy of the complex resulting in the rupture of the van-der-Waals bond, and the excess energy is distributed among the vibration-rotation-translational degrees of freedom of the fragments. The $\Delta v = 1$ and $\Delta v = 2$ emission from the HF fragment are then detected by large area PbS and Ge detectors, respectively. For the bands presently examined $v_1 = 3, v_2 = 0$ of $(\text{HF})_2$ and the analogous band of HFHCl , the channel with the HF fragment in the $v = 2$ level is the more dominant one, as expected from $\Delta v = -1$ propensity rules.

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RF01 15 min 1:30

THE INFRARED SPECTRUM OF CF_3^+ TRAPPED IN SOLID NEON. DANIEL FORNEY AND MARILYN E. JACOX

When a $\text{Ne}:\text{CF}_4$ sample is codeposited at approximately 5 K with a beam of neon atoms that has been excited in a microwave discharge, the absorption near 1665 cm^{-1} which has previously been assigned to ν_3 of CF_3^+ formed from other precursor molecules is observed. The $(\nu_1 + \nu_4)$ combination band of CF_3^+ , obscured by the nearby H_2O absorption in the earlier argon-matrix studies, is detected at 1625.1 cm^{-1} . In addition, the out-of-plane deformation fundamental of CF_3^+ is observed. The CF_3^+ assignments are supported by the results of similar experiments in which HCF_3 or DCF_3 is substituted for CF_4 .

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RF02 15 min 1:47

THE INFRARED SPECTRA OF BF_2 , BF_2^+ , AND BF_3^+ TRAPPED IN SOLID NEON. MARILYN E. JACOX AND WARREN E. THOMPSON

When a $\text{Ne}:\text{BF}_3$ sample is codeposited at approximately 5 K with a beam of neon atoms that has been excited in a microwave discharge, all three vibrational fundamentals and the $(\nu_1 + \nu_3)$ combination band of BF_2 are identified. The ν_3 absorption of BF_2^+ is also present. The positions of these absorptions are close to those obtained in recent *ab initio* calculations.¹ Other new absorptions can be assigned to BF_3^+ , which photodissociates in the red spectral region.

1. K. K. Irikura and J. W. Hudgens, private communication.

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RF03

15 min

2:04

Electronic structure, effective spin Hamiltonian expressions, and experimental evidence for the parallel electron paramagnetic resonances of matrix-isolated $(\eta^6\text{-C}_6\text{H}_6)\text{V}$ and $(\eta^6\text{-C}_6\text{D}_6)\text{V}$ half-sandwich complexes.
Saba M. Mattar, Ramaswami Sammynaiken and Israel Unger

Benzene and perdeutrobenzene are reacted with vanadium atoms and matrix-isolated in Ar at 12 K. The resulting $(\eta^6\text{-C}_6\text{H}_6)\text{V}$, $(\eta^6\text{-C}_6\text{D}_6)\text{V}$, $(\eta^6\text{-C}_6\text{H}_6)_2\text{V}$, and $(\eta^6\text{-C}_6\text{D}_6)_2\text{V}$ compounds are investigated by electron paramagnetic resonance (EPR) spectroscopy. The EPR spectra are well resolved and the parallel features of the resonances due to the g_{zz} , $a_{zz}(^{51}\text{V})$, and $a_{zz}(^1\text{H})$ tensor components are identified experimentally for the first time. Spectral features of $(\eta^6\text{-C}_6\text{H}_6)\text{V}$ and $(\eta^6\text{-C}_6\text{D}_6)\text{V}$, such as the resonance field positions and intensities, are all analyzed and accounted for by computer simulation. The effective spin Hamiltonian tensor components and resonance field positions are derived in terms of their molecular orbital coefficients. The magnetic properties, such as the g , hyperfine and superhyperfine tensor components are compared with those computed using the local-density-functional (LDF) approximation. Both the experimental spectra and electronic structure computations confirm that the $(\eta^6\text{-C}_6\text{H}_6)\text{V}$ and $(\eta^6\text{-C}_6\text{D}_6)\text{V}$ complexes have 2A_1 ground states.

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RF04

15 min

2:21

ELECTRONIC AND VIBRATIONAL ABSORPTION SPECTRA OF THE TETRACENE AND PENTACENE RADICAL CATIONS ISOLATED IN ARGON MATRICES

J. Szczepanski, C. Wehlburg, J. Drawdy and M. Vala

The low energy electron impact technique has been employed to ionize tetracene and pentacene in an Ar or Ar/0.1% CCl_4 gas phase mixture. The electron bombardment products were deposited and stabilized in an argon matrix at 12K. An intensity correlation between the 392nm(tetracene) or 954nm (pentacene) electronic bands due to the radical cations and the newly observed vibrational bands was sought by varying the ratio of the abundance of tetracene or pentacene cations to all other species in the matrix. For these, and other polycyclic aromatic hydrocarbons reported earlier¹, the intensity distribution of the IR bands is significantly different from the intensity distribution of the neutral parents.

The analysis of the vibrational energy shifts versus local charge density values for some normal modes for the series of linear polycyclic aromatic hydrocarbon cations from naphthalene to pentacene will be presented.

¹J. Szczepanski and M. Vala, *Astrophys. J.* **414**, 646 (1993).

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RF05

15 min

2:38

INTERNAL IONIZATION OF Ar AND Kr NOBLE-GAS CRYOCRYSTALS BY MATRIX-ISOLATED He METASTABLE EXCITED ATOMS, R.A.ZHITNIKOV AND YU.A.DMITRIEV

Local metastable excited states are found in Ar and Kr cryocrystals as the He metastable excited atoms traps in the growing cryocrystals. These states are detected by ESR and interpreted as being 3P_2 atom-like local excited states in Ar and Kr cryocrystals. The study shows that the yield of the 3P_2 excitations in the above process decreases with temperature increasing. Analysis of the results allows the following explanation of the effect observed to be given. He metastable excited atoms trapped in the growing Ar or Kr cryocrystals transfer their excitation energy to the cryocrystal to form, in the process of internal ionization, an ion Rg^+ and a free electron, whereupon the fast (of 10^{-12} s) self-trapping reaction of the hole follows: $Rg^+ + Rg \rightarrow Rg_2^+$. Thereafter, either the dissociative recombination reaction $Rg_2^+ + e \rightarrow Rg_2^{**} \rightarrow Rg + Rg(^3P_2) + \Delta E$ or recombination $Rg_2^+ + e \rightarrow Rg_2^{**} \rightarrow Rg + Rg + \Delta E$ to produce ground-state atoms could take place. The former is likely at lower temperatures while the latter - at higher ones when the vibrational relaxation rate of the Rg_2^{**} molecule increases. This is the reason for the observed temperature dependence.

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RF06

15 min

2:55

INFRARED SPECTRA OF THE HYDROXYSULFONYL RADICAL $HOSO_2$ (THE PRECURSOR TO ACID RAIN) AND SULFURIC ACID IN SOLID ARGON AT 12 K.

FRED PERRY, TAMMY M. JENKINS, AND FRANK T. PROCHASKA

Hydroxyl radicals produced by a microwave discharge of water vapor at high dilution in argon were deposited with a mixture of sulfur dioxide and argon onto a cesium iodide window maintained at 12 K. The major products, formed on the surface of the condensing argon matrix, were the previously-reported HSO_2^- anion, the $HOSO$ radical, and the hydroxysulfonyl radical $HOSO_2$. Five previously-unreported infrared absorptions of $HOSO_2$ were observed, allowing assignment of all nine vibrational frequencies of this molecule, which is the precursor to acid rain. Warming the matrix to allow diffusion caused significant growth of the hydroxysulfonyl radical absorptions; in addition, infrared bands due to sulfuric acid molecules appeared in the spectrum after diffusion. Oxygen-18 isotopic substitution data are reported for the first time for these two molecules.

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RF07 5 min 3:12

INFRARED SPECTRUM OF S_2O_2 IN SOLID ARGON. G. Dana Brabson and Lester Andrews.

Codeposition of O_2 with the superheated vapors of sulfur from a Knudsen cell yields a new isomer of S_2O_2 in which both the S_2 and O_2 moieties are retained. The two bands, 1403 and 725 cm^{-1} , are assigned to the O-O and S-S motions, respectively. Experiments with scrambled isotopes (O-16/O-18 and S-32/S-34) confirm the presence of the S_2 and O_2 fragments. In each case, a triplet of very narrow lines is obtained, suggesting that the vibrational coupling between the two fragments is minimal and/or that the two atoms in each fragment are equivalent. Upon photolysis ($\lambda > 200\text{ nm}$), S_2O and a perturbed SO_2 (1347 , 1147 , and 519 cm^{-1}) are obtained.

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RF08 15 min 3:18

INFRARED SPECTRA OF SELENIUM OXIDES IN SOLID ARGON. G. Dana Brabson and Lester Andrews.

Codeposition of O_2 with the superheated vapors of selenium from a Knudsen cell yields Se_2O_2 , with bands at 1404, 391 and 361 cm^{-1} . The presence of the O_2 fragment is confirmed by scrambled O-16/O-18 experiments; a triplet with very narrow lines is obtained, suggesting that the two oxygens are equivalent and/or poorly vibrationally coupled to the Se_2 moiety. The presence of the Se_2 fragment is suggested by the locations of the observed bands, the subsequent chemistry in the matrix, and the correspondence with the sulfur-oxygen system, in which S_2O_2 is found. Subsequent photolysis at $\lambda > 490\text{ nm}$ yields SeO (883 cm^{-1}), $(SeO)_2$ (the van der Waals dimer, 875 cm^{-1}), $SeO_2\cdot Se$ (perturbed SeO_2 , 960, 921, 365 cm^{-1}), and $SeOSeO$ (966, 636, and 294 cm^{-1}). In each of these product molecules, the individual lines due to the selenium isotopes, occurring in natural abundance, are resolved. Codeposition of O_3 with the superheated selenium vapors yields, in addition to SeO , a broad band which is assigned to Se_2O (903 cm^{-1}); this feature is also obtained when one traps the products of a microwave discharge in argon seeded with oxygen and selenium vapor.

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RF09

5 min

3:35

INFRARED SPECTRA OF S_2NO AND Se_2NO IN SOLID ARGON. G. Dana Brabson and Lester Andrews.

Codeposition of NO with the superheated vapors of chalcogens from Knudsen cells yields S_2NO (1771.7 and 670 cm^{-1}) and Se_2NO (1771.1 cm^{-1}). The chalcogen-chalcogen stretching frequencies are surprisingly close, and are less than 5 cm^{-1} to the low-energy side of the $(NO)_2$ band. Convincing proof that the new bands belong to a new molecule (and not to a perturbed $(NO)_2$ species) is provided by scrambled N-14/N-15 and O-16/O-18 experiments. Products of photolysis include the better known oxides, S_2O , SeO , and Se_2O .

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RF10

15 min

3:41

INFRARED ABSORPTION OF CIS-CIS PEROXYNITROUS ACID ($HOONO$) IN SOLID ARGON, WEN-RAY LO AND YUAN-PERN LEE

Nitric acid ($HONO_2$) isolated in solid argon at 12 K was irradiated with 193-nm emission from an ArF excimer laser. Recombination of photofragments OH and NO_2 led to the formation of various conformers of peroxyxynitrous acid ($HOONO$). In addition to the previously reported lines due to cis-perp $HOONO$,¹ lines at 3285.4, 1600.3, 1395.0, 927.2, 794.3, and 616.9 cm^{-1} were observed; they are assigned to cis-cis $HOONO$. The observed vibrational frequencies and the ^{15}N isotopic shifts of both conformers are in agreement with recent theoretical calculations. The cis-cis $HOONO$ was photolyzed much more rapidly than the cis-perp $HOONO$ upon irradiation of the 308-nm emission from the XeCl laser. The mechanism of formation of different conformers of $HOONO$ are discussed.

1. B.-M. Cheng, J.-W. Lee and Y.-P. Lee, J. Phys. Chem. **95**, 2814 (1991).

Address of Lee: Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan 30043.

RF'01 15 min 4:15

THE MILLIMETER AND SUBMILLIMETER-WAVE SPECTRUM OF THE TORSIONAL STATES OF HOOH IN THE GROUND, ν_3 , AND ν_6 VIBRATIONAL STATES.

D. T. PETKIE, T. M. GOYETTE, P. A. HELMINGER, AND F. C. DE LUCIA

Hydrogen peroxide is the simplest molecule that can execute torsional motion, and as a light asymmetric rotor has substantial centrifugal distortion contributions to its rotational-torsional spectrum. The spectrum and analysis of HOOH includes the $n = 0$ and $n = 1$, $\tau = 1, 2$ and $\tau = 3, 4$ torsional states. In addition, transitions between the $n=0$ torsional sublevels in ν_3 , and ν_6 have been measured. The ground state analysis is a combined fit that includes recent infrared data^{1,2} with the microwave data. The model uses the Watson A-reduced Hamiltonian and includes a fermi resonance interaction between the torsional states. Both sets of data are fit to their respective uncertainties. The results of this analysis will be presented, along with the assignments for the ν_3 and ν_6 transitions.

1. W. B. Olson, R. H. Hunt, B. W. Young, A. G. Maki, and J. W. Brault, *J. Mol. Spectrosc.* **127**, 12-34 (1988)
2. C. Camy-Peyret, J. -M. Flaud, J. W. C. Johns, and M. Noel, *J. Mol. Spectrosc.* **155**, 84-104 (1992)

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Address of Helming: Department of Physics, University of South Alabama, Mobile, AL 36688

RF'02 15 min 4:32

THE ROTATIONAL SPECTRUM OF TRANS ETHANOL (CH₃CH₂OH)

K. V. L. N. SASTRY, J. C. PEARSON, M. M. BEAKY, L. C. OESTERLING, ERIC HERBST AND FRANK C. DE LUCIA

The spectrum of the double internal rotor ethanol ($\nu_{OH} = 0, 1, 2, \dots$; $\nu_{CH_3} = 0, 1, 2, \dots$ of internal rotation) has been studied in the millimeter-wave region. Approximately 200 lines have been assigned to the lowest trans state ($\nu_{OH}(A) = 0$, $\nu_{CH_3}(A,E) = 0$) and a few have been tentatively assigned to the lowest gauche states ($\nu_{OH}(E+, E-) = 0$, $\nu_{CH_3}(A,E) = 0$). A three-fold internal rotor analysis of the methyl rotation in the trans state will be presented including previous data¹. Formulation of a complete molecular Hamiltonian² and the selection rules for the ground torsional state ($\nu_{CH_3} = \nu_{OH} = 0$) will be discussed.

¹F. J. Lovas *J. Phys. Chem. Ref. Data*, **11**, 251-276 (1982).

²Ramesh K. Kakar and C. Richard Quade, *J. Chem. Phys.*, **72**, 4300-4307 (1980).

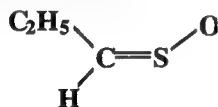
Addresses of Pearson, Beaky, Oesterling, Herbst, and De Lucia: Department of Physics, The Ohio State University, 174 W. 18th. Ave., Columbus, OH 43210.

Address of Sastry: Department of Physics, University of New Brunswick, Fredericton, New Brunswick, E3B 5A3.

RF'03 15 min 4:49

FT MICROWAVE CHARACTERIZATION OF THE ONION LACHRYMATOR (Z)-PROPANETHIAL S-OXIDE GENERATED BY A FLOW PYROLYSIS, J. Z. GILLIES, C. W. GILLIES, H. E. WARNER, AND R. MALLOY

The microwave spectra of (Z)-Propanethial S-Oxide (ethyl sulfine) isotopomers, C_2H_5CHSO and $C_2H_5CH^{34}SO$, were assigned using pulsed beam FT microwave spectroscopy. Ethyl sulfine, the species responsible for onion tears, has been generated via an on-line pyrolysis in which the precursor, 2-methyl-2-propyl vinyl sulfoxide, was flowed through a furnace coupled directly to the pulsed nozzle. Rotational constants (in MHz) obtained from a fit of *a*- and *b*-type transitions to a Watson Hamiltonian are $A=10182.258(3)$, $B=2209.567(1)$, $C=1997.111(1)$ for the normal species, and $A=10113.393(2)$, $B=2181.858(1)$, and $C=1972.327(1)$ for the sulfur-34 isotope. The isotopic moments of inertia are consistent with a planar C-C-S-O framework in which the oxygen and the ethyl group are syn to each other with respect to the C-S bond.



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RF'04 15 min 5:06

Precise Rotational and Hyperfine Parameters of Nitrosyl Chloride Obtained Using a Cavity Pulsed Microwave Fourier Transform (MWFT) Spectrometer

Bethany Gatehouse, Holger S.P. Müller, Nils Heineking, and Michael C.L. Gerry

The pure rotational spectra of 5 isotopic species of nitrosyl chloride, $^{35}Cl^{14}N^{16}O$, $^{37}Cl^{14}N^{16}O$, $^{35}Cl^{15}N^{16}O$, $^{37}Cl^{15}N^{16}O$ and $^{35}Cl^{14}N^{18}O$, have been measured using a cavity pulsed microwave Fourier Transform spectrometer. The high sensitivity of this spectrometer allowed us to measure *a*-type spectra of all 5 isotopomers in natural abundance. We have also observed weak *b*-type spectra of the first four isotopomers, the latter three of these for the first time. An enriched sample was used to measure *b*-type transitions for the ^{15}N isotopomers. Precise values for the rotational constants and the quartic centrifugal distortion constants have been obtained, and the centrifugal distortion constants have been used in a refinement of the harmonic force field.

The hyperfine structures show small effects (up to ~ 50 kHz) arising from spin-rotation coupling and somewhat larger effects (up to ~ 1.5 MHz) arising from accidental near-degeneracies of the rotational energy levels. These deviations have allowed us to calculate spin-rotation constants and off-diagonal quadrupole coupling constants, χ_{ab} , for both Cl and N. The quadrupole coupling tensors have been diagonalized.

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Address of Heineking: Walther-Nernst-Institut, Humbolt-Universität zu Berlin, Berlin, Germany

RF'05 15 min 5:23**MICROWAVE FOURIER TRANSFORM SPECTROSCOPY OF SULFURYL CHLORIDE FLUORIDE, SO_2ClF :
STRUCTURE, HYPERFINE CONSTANTS, AND HARMONIC FORCE FIELD**HOLGER S. P. MÜLLER AND MICHAEL C. L. GERRY

The pure rotational spectrum of sulfonyl chloride fluoride, SO_2ClF , has been investigated in the frequency range 5.6 - 24.0 GHz using a pulsed molecular-beam microwave Fourier transform spectrometer. Between 48 and 150 lines of 8 to 25 rotational transitions have been observed for the six isotopomers SO_2ClF , $\text{SO}_2^{37}\text{ClF}$, $^{34}\text{SO}_2\text{ClF}$, $^{34}\text{SO}_2^{37}\text{ClF}$, $\text{SO}^{18}\text{OClF}$, and $\text{SO}^{18}\text{O}^{37}\text{ClF}$ (unlabeled atoms indicate ^{16}O , ^{19}F , ^{32}S , and ^{35}Cl) in natural isotopic abundance. The rotational and quartic centrifugal distortion constants have been determined. r_0 , r_{AP} , and r_s -type structural parameters have been evaluated. A harmonic force field has been calculated in order to derive ground state average and estimated equilibrium bond lengths. Chlorine and fluorine hyperfine structures have been resolved, allowing quadrupole coupling (including χ_{bc} for the isotopomers containing ^{18}O) and spin-rotation constants to be determined. Variations of the chlorine quadrupole coupling constants with different isotopomers have allowed the quadrupole tensor to be diagonalized, and indicate χ_{zz} to coincide with the SCI bond.

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B. C., Canada V6T 1Z1

RG01 30 min 1:30**CALCULATED SPECTROSCOPIC PROPERTIES FOR NEGATIVE MOLECULAR IONS AND CLUSTER IONS**

P. Botschwina

Large-scale ab initio calculations, mainly at the CEPA-1¹ and CCSD(T)² levels, were carried out for a number of negative molecular ions like NO₂⁻, NCO⁻, HCC⁻, CH₂N⁻, BH₃⁻, CCl₃⁻, HCCO⁻, CH₂CN⁻ and CH₂NC⁻. HCC⁻ exhibits a shallow energy minimum in the T-shaped configuration. High-lying rovibrational states with energies in the vicinity of the barrier to isomerization are discussed in detail. The vibrational structure of the first bands of the photoelectron spectra of CH₂N⁻, BH₃⁻ and CCl₃⁻ has been calculated within the Franck-Condon approximation. Comparison with experiment will be made for the first two species. HCCO⁻ is calculated to have a non-linear equilibrium structure with a small barrier to linearity of 272 cm⁻¹ (CCSD(T)/151 cGTOs). The potential energy hypersurface for the isomerization process CH₂NC⁻ → CH₂CN⁻ is discussed.

In addition, the cluster anions F⁻...CH₃F, Cl⁻...CH₃F and Cl⁻CH₃Cl were studied. Their formation is accompanied by a substantial increase in the intensities of the C-Hal vibrations. E. g., the CCl (ν₃) vibration in Cl⁻...CH₃Cl is red-shifted by 93 cm⁻¹ and gains in intensity by a factor of 6 compared to free CH₃Cl.

¹CEPA-1: Coupled Electron Pair Approximation, version 1; W. Meyer, *J. Chem. Phys.* **58**, 1017 (1973).

²Coupled Cluster method with single and double excitation operators and a quasiperturbative treatment of the effects of connected triple excitations; K. Raghavachari, G. W. Trucks, J. A. Pople and M. Head-Gordon, *Chem. Phys. Lett.* **157**, 479 (1989).

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RG02 15 min 2:05**ACCURATE AB INITIO POTENTIAL SURFACES OF AR-HF, AR-H₂O, AND AR-NH₃, FU-MING TAO and W. KLEMPERER**

We present accurate potential energy surfaces for Ar-HF, Ar-H₂O, and Ar-NH₃ from the supermolecular calculations using Møller-Plesset perturbation theory up to the complete fourth-order (MP4) and efficient basis sets containing bond functions. The calculations on Ar-HF with a fixed HF bond length of $r = \langle r \rangle_{v=0}$ give a global potential minimum with a well depth of 200.0 cm⁻¹ at the position $R = 3.470$ Å, $\theta = 0^\circ$ (linear Ar-H-F), a secondary minimum with a well depth of 88.1 cm⁻¹ at $R = 3.430$ Å, $\theta = 180^\circ$ (linear Ar-F-H), and a potential barrier of 128.3 cm⁻¹ that separates the two minima near $R = 3.555$ Å, $\theta = 90^\circ$ (T-shaped). Further calculations on the three main configurations of Ar-HF with varying HF bond length are carried out to obtain vibrationally averaged well depths for $v = 0, 1, 2$, and 3. Our primary wells are about 15 cm⁻¹ higher than those of Hutson's H6(4,3,2) potential¹ for $v = 0, 1, 2$, and 3, and our minimum distances are about 0.05 Å longer. The intermolecular potentials of Ar-H₂O and Ar-NH₃ are calculated with the monomers held fixed at equilibrium geometry. The calculations on Ar-H₂O give a single global minimum with a well depth of 130.2 cm⁻¹ at $R = 3.603$ Å, $\theta = 75^\circ$, $\phi = 0^\circ$, along with barriers of 22.6 and 26.6 cm⁻¹ for in-plane rotation at $\theta = 0^\circ$ and 180° respectively, and a barrier of 52.6 cm⁻¹ for out-of-plane rotation at $\theta = 90^\circ$, $\phi = 90^\circ$. All these agree well with experiment, especially with the recent AW2 potential.² The calculations on Ar-NH₃ give a single global minimum with a well depth of 130.1 cm⁻¹ at $R = 3.628$ Å, $\theta = 90^\circ$, $\phi = 60^\circ$, along with barriers of 55.2 and 38.0 cm⁻¹ for end-over-end rotation at $\theta = 0^\circ$ and 180° respectively, and a barrier of 26.6 cm⁻¹ for rotation about NH₃ symmetry axis at $\theta = 90^\circ$, $\phi = 0^\circ$. Again, all these agree with experiment.³

1. J.M. Hutson, *J. Chem. Phys.* **96**, 6752 (1992).

2. R.C. Cohen and R.J. Saykally, *J. Chem. Phys.* **98**, 1007 (1993).

3. C.A. Schmuttenmaer, R. Cohen, and R.J. Saykally, *J. Chem. Phys.*, submitted.

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RG03 15 min 2:22

**METALLOAROMATIC STABILIZATION OF METALLOCARBOHEDRENES, CLINTON S. NASH,
BRUCE E. BURSTEN**

Since their detection by mass spectrometry¹, metallocarbohedrenes ('met-cars') of the general formula M_8C_{12} ($M = Ti, V, Hf, Zr$, etc.) have been the subject of numerous investigations. The most widely accepted idealized structure of met-cars is a T_h structure analogous to the unknown icosahedral fullerene, C_{20} . We have used local density functional calculations to investigate the stability of $T_h M_8C_{12}$ vis-à-vis the likely instability of C_{20} . Results indicate that the twenty-membered fullerene is subject to anti-aromatic destabilization resulting from the partial population of a π -antibonding HOMO. By contrast, the presence of energetically accessible metallic d orbitals in met-cars is seen to alleviate this effect by converting this non-bonding/antibonding HOMO to a purely bonding orbital, an interaction analogous to metalloaromaticity. It is further seen that striking parallels exist between the electronic structure of metallocarbohedrenes and that of C_{60} , and that these similarities constitute an alternative description of the met-cars that sheds light on their stability.

1. Guo, B.C.; Kerns, K.P.; Castleman, A.W. Jr.; Science **1992**, 255. 1411.

Address of Bursten and Nash: Department of Chemistry, The Ohio State University, Columbus, OH. 43210.

RG04 15 min 2:39

Excited Potential Energy Surfaces of CH_3SH From the *Ab Initio* Effective Valence Shell Hamiltonian Method. Jonathan E. Stevens, Richard L. Graham, Karl F. Freed, and Michael F. Arendt, The James Franck Institute and the Department of Chemistry, The University of Chicago, Chicago Illinois 60637.

The ground and first and second $^1A''$ surfaces of methyl mercaptan (CH_3SH) are calculated as a function of the C-S and S-H bond coordinates using the *ab initio* effective valence shell Hamiltonian (\mathcal{H}^v) method. These computations provide the first serious tests for choosing restricted valence spaces and for computing global potential energy surfaces with the \mathcal{H}^v methods. The global surfaces are computed with a modest basis, but larger basis set computations at selected geometries test convergence for vertical excitation energies, ionization potentials, and C-S and S-H bond energies. The calculations assist in the interpretation of CH_3SH photodissociation dynamics observed by Butler and co-workers¹.

1. J.S. Keller, P.W. Kash, E. Jensen, and L.J. Butler, J. Chem. Phys. 96, 4323 (1992); E. Jensen, J.S. Keller, G.C.G. Washewsky, J.E. Stevens, R.L. Graham, K.F. Freed, and L.J. Butler, J. Chem. Phys. 98, 2882 (1993).

RG05 15 min 2:56

AB INITIO CALCULATIONS OF STRUCTURE AND VIBRATIONAL SPECTRA OF THE ALUMINUM OXIDE MOLECULES. A.V.NEMUKHIN

The results of previous^{1,2} and current theoretical studies of structural and vibrational properties of aluminum oxides are discussed. The species Al_nO_m ($n=1,2$, $m=1-4$) have been considered. Calculations have been performed at the SCF and MP2 levels with the 3-21G, 6-31G* basis sets as well as with a specially designed basis suitable for a treatment of these essentially ionic compounds. GAUSSIAN 90 and GAMESS quantum chemistry packages have been used for computations. A detailed comparison has been carried out with the results of experimental investigations of matrix-isolated products of $Al + O_2$ reactions^{2,3}.

-
1. A.V.Nemukhin, and F.Weinhold, J.Chem.Phys. 97, 3420 (1992)
 2. A.V.Nemukhin, and L.V.Serebrennikov, Russ.Chem.Rev.62,527(1993)
 3. L.Andrews, T.R.Burkholder, and J.T.Yustein, J.Phys.Chem. 96, 10182 (1992)
-

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RG06 10 min 3:13

HSIN: CALCULATED SPECTROSCOPIC PROPERTIES AND BARRIER HEIGHT TO ISOMERIZATION FOR HSIN

P. Botschwina, M. Oswald and E. Schick

Quite recently, the matrix-isolation IR spectrum of HSiN was reported by Maier and Glatthaar.¹ They observed the stretching vibrations of $H^{28}SiN$ and $D^{28}SiN$ (in parentheses) at 2152.2 (1580.5) and 1162.2 (1145.4) cm^{-1} . We have carried out CCSD(T)² and internally contracted MRCI³ calculations. The former yielded $\nu_1 = 2117$ (1563), $\nu_2 = 157$ (117) and $\nu_3 = 1129$ (1117) cm^{-1} . The barrier height (BH) for isomerization to the more stable HNSi species was obtained to be 4107 cm^{-1} (MRCI). CCSD(T) calculations yield a slightly lower value of 3927 cm^{-1} while MP2⁴ performs poorly (BH: 14015 cm^{-1}).

¹G. Maier and J. Glatthaar, Angew. Chem. 106, 486 (1994).

²Coupled Cluster method with single and double excitation operators and a quasiperturbative treatment of the effects of connected triple excitations; K. Raghavachari, G. W. Trucks, J. A. Pople and M. Head-Gordon, Chem. Phys. Lett. 157, 479 (1989).

³MRCI: Multiconfiguration reference configuration interaction; H.-J. Werner and P. J. Knowles, J. Chem. Phys. 89, 5803 (1988).

⁴Second-order perturbation theory according to Møller and Plesset.

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RG07 5 min 3:25
THE EQUILIBRIUM GEOMETRIES OF C₅ AND C₃

P. Botschwina

Making use of large-scale CCSD(T)-calculations¹ the equilibrium geometry of C₅ was calculated to be linear with R_{1e} (outer CC) = 1.28959 Å and R_{2e} (inner CC) = 1.28190 Å, with uncertainties of ca. 0.0005 Å. The corresponding equilibrium rotational constant is B_e = 2550.6 MHz, in good agreement with an approximate experimental value of 2548.7 MHz.²

Analogous calculations for C₃ yield a linear equilibrium structure with R_e = 1.29431 Å; for C₂ a value of 1.24209 Å is obtained. The latter differs from experiment³ by 0.0004 Å.

¹Coupled Cluster method with single and double excitation operators and a quasiperturbative treatment of the effects of connected triple excitations; K. Raghavachari, G. W. Trucks, J. A. Pople and M. Head-Gordon, Chem. Phys. Lett. **157**, 479 (1989).

²N. Moazzen-Ahmadi, S. D. Flatt and A. R. W. McKellar, Chem. Phys. Lett. **186**, 291 (1991).

³K. P. Huber and G. Herzberg, Molecular Spectra and Molecular Structure, IV. Constants of Diatomic Molecules, Van Nostrand, New York, 1979.

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INTERMISSION

RG08 10 min 3:50
AN AB INITIO CALCULATION OF THE RENNER EFFECT IN CH₂⁺

W. P. KRAEMER, PER JENSEN AND P.R. BUNKER

We report the results of an *ab initio* calculation of vibronic (i.e. $N = 0$) energy levels of the CH₂⁺ molecular ion giving the lowest 19 levels of the ground \tilde{X}^2A_1 electronic state and the lowest 15 of the first excited \tilde{A}^2B_1 state. At the linear configuration these states become degenerate ($^2\Pi$); the \tilde{X} state is calculated to be bent at equilibrium with a barrier to linearity of 1089 cm⁻¹, and the \tilde{A} state is calculated to be linear at equilibrium. The potential energy surfaces were calculated over a wide range of nuclear geometries using the multi-reference configuration interaction (MR-CI) level of theory with molecular orbital bases that were optimized separately for each state by complete-active-space SCF (CASSCF) calculations. The MOLCAS-1 programme system was used. The vibronic energies were calculated variationally using the Morse Oscillator Rigid Bender Internal Dynamics (MORBID) programme modified to include the effect of electronic angular momentum (the Renner effect). Results for CD₂⁺ and CHD⁺ will also be reported, and it is hoped that we will be able to report preliminary results for $N > 0$ levels.

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RG09

15 min

4:02

VIBRATION-ROTATION SPECTRA OF H_3^+ AND ITS D ISOTOPES: A SUMMARYJ. K. G. WATSON

A large number of lines of all H and D isotopes of the H_3^+ molecular ion have now been assigned. The use of vibration-rotation calculations starting from a good *ab initio* potential¹ was of great value in assigning many of the lines, particularly those involving higher vibrational and rotational levels. Another good *ab initio* potential² has become available more recently. With slight adjustments to some of the *ab initio* potential coefficients it is possible to assign many more lines. The present work summarises the potentials obtained by fitting the different isotopes independently, and considers evidence from the isotope effects for the breakdown of the Born-Oppenheimer approximation.

¹ W. Meyer, P. Botschwina and P. Burton, *J. Chem. Phys.* **84**, 891-900 (1986).

² G. C. Lie and D. Frye, *J. Chem. Phys.* **96**, 6784-6790 (1992).

Address of Watson: Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6

RG10

10 min

4:19

THEORETICAL ANALYSIS OF H_3^+ VIBRATIONAL STATES,NICHOLAS G. FULTON, GONZALO POLAVIEJA, AND JONATHAN TENNYSON

In 1984 Carrington and Kennedy¹ published a predissociation spectrum of H_3^+ . With nearly 27 000 lines in a 220 cm^{-1} window at about 1000 cm^{-1} from the origin, the very complicated structure has yet to be explained. On Gaussian smoothing of the highest transition four broad peaks arose, separated by about 30 cm^{-1} .

Classical trajectory analysis by Gomez Llorente and Pollak² suggested that asymmetric excitation of the horseshoe bending mode is responsible along with rotational excitation to explain the separation of the peaks. Quantal and semi-classical calculations have confirmed the existence of the horseshoe states, but have yet to uncover the excited horseshoes. The sheer size of the calculation necessary means that only recently with the advent of ever more powerful computers are realistic attempts being made to recreate the spectrum from purely theoretical grounds.

The results presented here are an analysis of H_3^+ wavefunctions using Husimi distributions to uncover underlying vibrational motion in the states around the dissociation limit. The vectors are produced using a Discrete Variable Representation (DVR) method of Henderson, Tennyson and Miller³ in Jacobi coordinates. Classical calculations are also presented to compare with the quantum results, and to help predict the positions of localisation and scarring of the wavefunctions. We present results of localisation in the horseshoe, excited horseshoe, elephant's foot, and other periodic orbits.

1. A. Carrington and R.A. Kennedy, *J. Chem. Phys.* **81** 91 (1984).

2. J.M. Gomez Llorente and E. Pollak, *J. Chem. Phys.* **90** 5406 (1989).

3. J.R. Henderson, J. Tennyson and S. Miller, *J. Chem. Soc. Faraday Trans.* **86** 1963 (1990).

Address of Fulton and Tennyson: Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, UK.

Address of Polavieja: Departamento de Química, C-IX. Universidad Autónoma de Madrid, Cantoblanco. 28049 Madrid, Spain.

RG11 15 min 4:31

Fourfold Clusters of Rovibrational Energies in H₂Te Studied with an *ab initio* Potential Energy Function

Per Jensen, Yan Li, Gerhard Hirsch, Robert J. Buenker, Timothy J. Lee, and Igor N. Kozin

We report here a theoretical study of the cluster effect¹ (i.e., the formation of nearly degenerate, four-member groups of rotation-vibration energy levels at higher J and K_a values) in the H₂Te molecule.

As the initial step of the investigation, we have carried out an *ab initio* calculation of the potential energy surface for the electronic ground state of H₂Te by means of the CCSD(T) method. With this potential energy surface as input, we have then used the MORBID (Morse Oscillator Rigid Bender Internal Dynamics) program² to calculate the rotation-vibration energy spectrum of H₂¹³⁰Te and its isotopomers for $J \leq 40$. These calculations reproduce the few known vibrational energies for H₂Te and HDTe to within a few cm⁻¹. The cluster structures obtained for the vibrational ground state and the fundamental vibrational levels of H₂Te are found to be extremely similar to those determined previously for H₂Se³. In particular, we do not determine any significant displacement of the clusters towards lower J values relative to H₂Se. Hence the experimental observation of the cluster states in H₂Te will be at least as difficult as in H₂Se, for which the cluster effect has been experimentally verified⁴.

¹see I. N. KOZIN AND P. JENSEN, *J. Mol. Spectrosc.* **163**, 483–509 (1994) and references therein.

²P. JENSEN, *J. Mol. Spectrosc.* **128**, 478–501 (1988).

³see I. N. KOZIN AND P. JENSEN, *J. Mol. Spectrosc.* **161**, 186–207 (1993) and references therein.

⁴I. N. KOZIN, S. KLEE, P. JENSEN, O. L. POLYANSKY AND I. M. PAVLICHENKOV, *J. Mol. Spectrosc.*, **158**, 409–422 (1993).

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Address of Li, Hirsch, and Buenker: FB 9 – Theoretische Chemie, Bergische Universität – Gesamthochschule Wuppertal, D-42097 Wuppertal, Germany.

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Address of Kozin: Applied Physics Institute, Russian Academy of Science, Uljanov Street 46, 603 600 Nizhnii Novgorod, Russia.

RG12 15 min 4:48

AN ANALYSIS OF THE TORSIONAL STRUCTURE OF ISO, TRANS AND CIS BUTENE FROM AB INITIO POTENTIAL SURFACES M.L.Senent, D.C. Moule and Y.G. Smeyers

The torsional spectroscopic parameters of the ISO, TRANS and CIS varieties of butene were determined from fully and partially optimized *ab initio* calculations. For this purpose the energy of conveniently chosen conformations were fitted to a symmetry adapted double Fourier expansion in seven terms. The band positions were calculated by solving variationally the nuclear Hamiltonian by using G₃₆ symmetry eigenvectors as trial function. The spectroscopic parameters and the experimental frequencies were compared with the results obtained from RHF calculations performed with large basis set with d and f polarization orbitals and the additions of MP2 and MP4 corrections to the correlation energy. The expansion coefficients of the interaction terms in the potential surfaces are analyzed from the energies and the structural data of the nuclear conformations.

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Address of Smeyers: Instituto de Estructura de la Materia, CSIC, Serrano 123, Madrid 28006, Spain.

RG13 10 min 5:05

**AB INITIO STUDY OF THE ELECTRONIC SPECTRUM OF THE
NCl₂ RADICAL, Z. -L. Cai**

The equilibrium geometries, excitation energies, force constants and vibrational frequencies for the low-lying electronic states X ²B₁, ²A₁, ²B₂ and ²A₂ of the NCl₂ radical have been calculated at the MRSDCI/DZ+P level. Our calculations indicate that the X ²B₁→²A₂ transition may correspond to the $\tilde{X}\rightarrow\tilde{A}$ band system which lies between 275–314 nm in absorption spectrum of refs. [1,2]. Our calculated excitation energies for X ²B₁→²A₁ and X ²B₁→²A₂, vibrational frequencies for the X ²B₁ and ²A₂ states and the geometry for the X ²B₁ state are in agreement with available experimental data. The electronic transition dipole moments, oscillator strengths for the ²A₁→X ²B₁ and ²A₂→X ²B₁ transitions and radiative lifetimes for the ²A₁ and ²A₂ states are calculated based on the MRSDCI wavefunctions, predicting value of the radiative lifetime for the ²A₁ state also in reasonable agreement with experiment.

¹A. G. Briggs and R. G. W. Norrish, Proc. Roy. Soc. A **278**, 27 (1964).

²V. V. Azatyan *et al.*, Dokl. Phys. Chem. **249**, 1056 (1980).

Address: Group 325, Department of Chemistry, Nanjing University of Science and Technology, Nanjing 210014, People's Republic of China.

RG14 15 min 5:17

**A method for calculating tunneling splitting and isotope effects
in hydrogen-bonded molecules, Vasil K. Babamov**

A method for calculating hydrogen tunneling splitting in a molecule with an intramolecular hydrogen bond is presented and applied to selected systems. The method utilizes the analytical formula for tunneling splitting for a particle in a double-well potential linearly coupled to a low-frequency bath¹ and another previously developed treatment suitable for quadratic couplings². The method can be viewed as a simple extension of the usual normal-mode treatment of molecular vibrations to incorporate the large-amplitude proton motion. It highlights the surprisingly large role of the heavy-atom motion in the hydrogen-atom tunneling. Excellent results are obtained in tests against multidimensional numerical calculations on model systems. The method is used to calculate tunneling splittings and isotope effects in malonaldehyde and tropolone and to estimate the barrier sizes. The relation of the approach to the macroscopic electron-transfer and proton-transfer theories is discussed.

1. V. K. Babamov, Chem. Phys. Lett. **217**, 254 (1994)

2. V.K. Babamov and R. A. Marcus, J. Chem. Phys. **74**, 1790 (1981))

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RH01 10 min 1:30

GAS-PHASE INFRARED SPECTROSCOPY OF N₂O IN A COLLISIONALLY COOLED CELL AT 5 AND 10 K, K. A. ROSS, D. R. WILLEY, A. S. MULLIN, S. SCHOWEN, L. ZHENG AND G. FLYNN

With the use of a collisionally cooled cell we have observed the R(0), R(1) and R(2) lines of the 00⁰0 - 00⁰1 vibrational transition of N₂O at 5 and 10 K. The N₂O gas was cooled via collisions with helium atoms in a cryogenic cell and a tunable diode laser near 2224 cm⁻¹ was used to observe the transitions. Doppler widths were measured for each of these lines. To our knowledge this represents the first reported use of the collisional cooling technique in the infrared at liquid helium temperatures.

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RH02 10 min 1:42

TUNABLE DIODE LASER SPECTROSCOPY OF CH₃F IN AN EQUILIBRIUM CELL MAINTAINED AT 7.5 KELVINS, D. R. WILLEY, K. A. ROSS, V. DUNJKO, AND A. W. MANTZ

We report the infrared measurement of rotational and translational temperatures for CH₃F in the gas phase with a temperature of 16 Kelvins. This is accomplished by extending the collisional cooling technique originally developed for the microwave spectral region¹ to the infrared. We measured an RQ(J,0) feature centered at approximately 1475 wavenumbers (in cm⁻¹) in the v₂ and v₅ bands of CH₃F. The rotational temperature was determined by measuring relative intensities of low J transitions and comparing these results to those predicted by the rotational partition function. We utilized measurements of the absorption line width to calculate the translational temperature.

1. D. R. Willey, R. L. Crownover, D. N. Bittner and F. C. De Lucia, J. Chem. Phys. 89, 1923 (1988).

Address of Willey and Ross: Department of Physics, Allegheny College, Meadville, PA 16335

Address of Dunjko and Mantz: Department of Physics and Astronomy, Franklin and Marshall College, Lancaster, PA 17604-3003

RH03 15 min 1:54
THE $\nu_2+\nu_3$ and $\nu_2+\nu_3-\nu_2$ BANDS OF NITROGEN DIOXIDE:

A. Perrin J.-M. Flaud, C.Camy-Peyret, M. Herman, D. Hurtmans and G.Guelachvili.

The 6.2 μm band of nitrogen dioxide is the strongest infrared band of this molecule. Then it is important, for atmospheric purposes, to get high quality parameters not only for the (main) ν_3 band¹, but also for the (first hot) $\nu_2+\nu_3-\nu_2$ which appears clearly in the low frequency range of the 6.2 μm band.

Using new Fourier transform spectra recorded at Brussels and at Paris, it has been possible to perform a new analysis of the $\nu_2+\nu_3$ and $\nu_2+\nu_3-\nu_2$ bands of $^{14}\text{N}^{16}\text{O}_2$, located at 4.2 μm and 6.21 μm respectively. From the spin-rotation levels of the (011) state obtained from these analyses, a set of molecular parameters (vibrational band centers, rotational spin-rotation and coupling constants) for the {(030),(011)} interacting states has been determined using a Hamiltonian matrix which takes explicitly into account the (030) \leftrightarrow (011) Coriolis type interactions and the spin-rotation operators explicitly into account. Finally, the synthetic spectra of the $\nu_2+\nu_3$ and $\nu_2+\nu_3-\nu_2$ bands (line positions and intensities) were generated.

I. A. Perrin, A.M. Vasserot, J.-M. Flaud, C.Camy-Peyret, G.Guelachvili, A.Goldman, F.J.Murcray, and R.D.Blatherwick, J. Mol. Spectrosc. **154** 391-406 (1992).

Address of Perrin, Flaud, Camy-Peyret and Guelachvili: Laboratoire de Physique Moléculaire et Applications, CNRS, Université Pierre et Marie Curie, Tour 13, bte 76, 4 Place Jussieu, F-75252 PARIS, Cedex 05, France

Address of Herman and Hurtmans: Laboratoire de Chimie Physique Moléculaire CPi 160/09, Université Libre de Bruxelles, 50 Avenue F.D.Roosevelt, B-1050 Bruxelles, Belgium.

RH04 15 min 2:11
**FIRST ANALYSIS OF THE $3\nu_9-\nu_9$, $3\nu_9-\nu_5$ AND $3\nu_9-2\nu_9$ BANDS OF HNO_3 :
TORSIONAL SPLITTING IN THE ν_9 VIBRATIONAL MODE.**

A. Perrin, J.-M. Flaud, C.Camy-Peyret, B.P.Winnewisser, S.Klee, A.Goldman, F.J.Murcray, R.D.Blatherwick, F.S.Bonomo, D.G.Murcray, and C.P.Rinsland,

Using Fourier transform spectra recorded at Giessen University and at Denver University in the 25 μm and 12 μm spectral regions respectively, it has been possible to perform the first analysis of the $3\nu_9-2\nu_9$, $3\nu_9-\nu_5$ and $3\nu_9-\nu_9$ hot bands of HNO_3 located at 392.4 cm^{-1} , 409.8 cm^{-1} and 830.4 cm^{-1} respectively. An accurate description of the torsional splitting in the $\nu_9=3$ vibrational state was achieved, leading to the determination of the two torsional band centers $E_{\nu_9=3,1}=1288.8451\text{cm}^{-1}$ and $E_{\nu_9=3,2}=1288.9036\text{cm}^{-1}$ and to the first determination of the ν_9 torsional potential of HNO_3 .

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Address of Goldman, Murcray, Blatherwick, Bonomo, and Murcray: Department of Physics, University of Denver, Denver, CO 80208, USA

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RH05 15 min 2:28

THE MILLIMETER AND SUBMILLIMETER-WAVE SPECTRUM OF THE ν_5 AND $2\nu_9$ VIBRATIONAL STATES OF NITRIC ACID: HNO_3

C. D. PAULSE, L. C. OESTERLING, T. M. GOYETTE, P. A. HELMINGER, AND F. C. DE LUCIA

The millimeter-wave spectrum of nitric acid (HNO_3) in its ν_5 and $2\nu_9$ vibrational states has been studied. Data were taken using a TWT based broadband spectrometer. The ν_5 and $2\nu_9$ states exhibit a large perturbation from the ordinary Watson Hamiltonian due to a Fermi interaction between the energy levels. Additionally, the large torsional splitting of transitions following b-type selection rules was observed for the $2\nu_9$ vibrational state. An interesting effect arising from the mixing of the $2\nu_9$ and ν_5 energy levels is the large splitting of the b-type transitions of the ν_5 vibrational state. A smaller torsional splitting was observed for transitions following a-type selection rules in the Q-branch transitions of both ν_5 and $2\nu_9$. The results of our analysis will be presented and compared with the results of previous studies.

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RH06 15 min 2:45

THE 10 μm BANDS OF THE $^{17}\text{O}_3$ ISOTOPIC SPECIES OF OZONE:

D. Consalvo, A. Perrin J.-M. Flaud, C. Camy-Peyret, and A. Valentin.

Using Fourier transform spectra recorded at LPMA ($\lambda \sim 0.002 \text{ cm}^{-1}$, $P=0.3$, 0.5 and 0.9 torr, $L=1.15\text{m}$) of $\sim 64\%$ ^{17}O -enriched ozone, it has been possible to assign the $\{\nu_1, \nu_3\}$ bands of $^{17}\text{O}_3$ up to very high rotational quantum numbers. For this analysis, we used the ground state energy levels calculated from the (000) rotational constants obtained for $^{17}\text{O}_3$ in a recent microwave study performed by Colmont et al.⁽¹⁾.

Then, from the set of $\{(100), (001)\}$ rotational energy levels derived in this work, a set of molecular parameters (vibrational band centers, rotational and coupling constants) for the $\{(100), (001)\}$ interacting states has been determined using a Hamiltonian matrix which takes explicitly into account the $(100) \leftrightarrow (001)$ Coriolis-type interaction operator. Finally, using ν_1 and ν_3 theoretically derived calculated transition moment operators, a synthetic spectrum (line positions and intensities) of the ν_1 and ν_3 bands has been generated.

1.- J.-M. Colmont and J. Demaison, (Private communication).

Address of Consalvo:

Laboratoire de Physique des Lasers, CNRS, Université Paris XIII, Av J.-B. Clement, F-94430 Villetaneuse, France

Address of Perrin, Flaud, Camy-Peyret and Valentin: Laboratoire de Physique Moléculaire et Applications, CNRS, Université Pierre et Marie Curie, Tour 13, bte 76, 4 Place Jussieu, F-75252 Paris, Cedex 05, France

RH07 15 min 3:02

QUASI-LINEARITY IN HCCN: THE ν_2 SPECTRUM, W. C. ECKHOFF, C. E. MILLER, AND R. F. CURL

The high resolution infrared spectrum of the quasi-linear molecule HCCN in the region of its ν_2 CCN stretching fundamental was recently measured. At least six separate vibrational origins have been positively identified. Using combination differences and the lower state spectroscopic constants for the ground state and excited bending mode states derived by McCarthy and Gottlieb,¹ the lower state for each vibrational transition has been assigned. Unambiguous assignment of the upper states is complicated by the appearance of duplicate sets of transitions originating from the same lower states. The most likely cause for this occurrence is a Fermi resonance between ν_2 and $\nu_3+(\nu_4+\nu_5)^{0+}$ (in linear molecule notation) which gives intensity to the transitions to the combination level.

1. 48th OSU Spectroscopy Symposium, June 1993

Address of Eckhoff, Miller, and Curl: Department of Chemistry and Rice Quantum Institute, Rice University, Houston, TX 77251

INTERMISSION

RH08 10 min 3:40

HIGH RESOLUTION SPECTROSCOPIC STUDIES OF CH_2F_2 : THE ν_6 BAND AT 3014 cm^{-1} . M.N. DEO, R. D'CUNHA, AND A. WEBER

Fourier transform infrared spectra of methylene fluoride have been recorded with the BOMEM DA3.002 spectrometer at NIST with an apodized resolution of 0.004 cm^{-1} in the region of the CH stretching fundamentals. Assignments have been made for the asymmetric CH stretching band ν_6 centered at 3014 cm^{-1} . More than 400 lines have been assigned in this C-type perpendicular band with quantum numbers up to $J''_{\text{max}} = 16$ and $K''_{\text{max}} = 12$. The data have been fitted to Watson's A-type reduced Hamiltonian in the I' representation to obtain molecular parameters for the upper state. Evidence of perturbations beyond $J''_{\text{max}} = 16$, $K''_{\text{max}} = 10$ are discernible in the observed spectra. The ν_6 level is expected to be perturbed by the ν_1 fundamental level via Coriolis coupling through rotation about the a-axis. Attempts to include the effect of perturbations with the neighboring fundamental and combination levels are underway. The details of the analysis will be presented.

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Address of Weber: Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, MD, 20899.

RH09 10 min 3:52

HIGH RESOLUTION FTIR SPECTROSCOPY OF THE ν_9 BAND OF SULFINE, H_2CSO

D.-L. Joo, Dennis J. Clouthier, V. Lai, E. Ma, C. P. Chan and A. J. Merer

The rotational analysis of the ν_9 (CH_2 wagging) fundamental at 762 cm^{-1} of sulfine will be presented. Spectra of this transient molecule were obtained by flowing the products of the 700°C pyrolysis of dimethyl sulfoxide vapor through a multipass cell mounted on a Bomem DA3.002 spectrometer. The strong C-type fundamental has unperturbed rotational structure at low J and K_a , but interacts with the $2\nu_7$ level at higher rotational energies, through A- and B-axis Coriolis coupling. The general energy level scheme for the interacting levels will be discussed.

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RH10 10 min 4:04

FOURIER TRANSFORM EMISSION SPECTROSCOPY OF BF AND AlF **K.Q. ZHANG, B. GUO, Z. MORBI, F. CHARRON AND P.F. BERNATH**

The high resolution infrared emission spectra of gas phase BF and AlF were recorded at 1400°C using a Bruker IFS 120HR Fourier transform spectrometer. The rotationally resolved spectra were analysed, and spectroscopic constants were derived. Preliminary equilibrium constants for the ground state BF are:

$$\begin{array}{lll} \omega_e = 1402.1551(3)\text{ cm}^{-1}, & \omega_e x_e = 11.8209(2)\text{ cm}^{-1}, & \omega_e y_e = 0.05158(4)\text{ cm}^{-1}, \\ B_e = 1.516738(1)\text{ cm}^{-1}, & \alpha_e = 1.90482(3) \times 10^{-2}\text{ cm}^{-1}, & D_e = 7.0944(7) \times 10^{-6}\text{ cm}^{-1}. \end{array}$$

The analysis of AlF will also be presented.

Address: Centre for Molecular Beams and Laser Chemistry, Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1.

RH11 10 min 4:16

OBSERVATION AND ANALYSIS OF THE HIGH RESOLUTION INFRARED EMISSION SPECTRUM OF CaF

François M.R. Charron, B. Guo, K. Zhang, Z. Morbi, P. Bernath

The high resolution rotation-vibration emission spectrum of CaF has been recorded using the Bruker IFS 120HR spectrometer at the University of Waterloo. The CaF molecule was obtained by heating calcium difluoride to 1600°C in a high temperature furnace. Improved spectroscopic constants will be presented.

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RH12 10 min 4:28

The High Resolution Thermal Emission Spectra of InF and DF

Z. Morbi, T. Karkanis, M. Dulick, J.B. White, K.Q. Zhang, F. Charron, B. Guo, P. Bernath

The high resolution gas phase spectra of InF and DF were recorded with the Bruker IFS 120HR Fourier transform spectrometer at the University of Waterloo. The spectrum of InF was recorded in the region of 400-600 cm^{-1} with a helium cooled Si:B detector at a resolution of 0.006 cm^{-1} . The DF spectra were recorded in the region of 2200-3300 cm^{-1} at a resolution of 0.01 cm^{-1} . An InSb detector was used and a total of 20 scans were co-added to obtain the spectrum. Ro-vibrational data up to $v=12$ were obtained for InF and up to $v=3$ for DF. Sets of Dunham coefficients Y_{ij} and mass-reduced Dunham constants U_{ij} are determined. The spectra show evidence of Born-Oppenheimer breakdown.

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RH13 10 min 4:40

HIGH-RESOLUTION FT-IR EMISSION SPECTRA OF MgF AND BaF

B. Guo, B. Barber, K.Q. Zhang and P.F. Bernath

The high resolution infrared emission spectra of gas phase MgF and BaF have been recorded using a Bruker IFS 120HR spectrometer. Vibration-rotation bands from 1 - 0 to 7 - 6 for MgF and from 1 - 0 to 10 - 9 for BaF were measured for the ground $X^2\Sigma^+$ states. The Dunham coefficients of MgF have been derived as:

$$\begin{aligned} Y_{01} &= 0.51927199(16) \text{ cm}^{-1}, Y_{02} = -1.08235(21) \times 10^{-6} \text{ cm}^{-1}, Y_{10} = 720.14305(59) \text{ cm}^{-1}, \\ Y_{11} &= 4.7194(30) \times 10^{-3} \text{ cm}^{-1}, Y_{12} = 3.4505(47) \times 10^{-9} \text{ cm}^{-1}, Y_{20} = -4.26091(28) \text{ cm}^{-1}, \\ Y_{21} &= 1.79436(75) \times 10^{-5} \text{ cm}^{-1}, Y_{30} = 0.016581(51) \text{ cm}^{-1}, Y_{31} = -1.96(54) \times 10^{-8} \text{ cm}^{-1}, \\ Y_{40} &= -4.43(31) \times 10^{-5} \text{ cm}^{-1}. \end{aligned}$$

The analysis of the BaF spectra will also be presented.

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RH14 10 min 4:52

FAR INFRARED EMISSION SPECTRA OF CsI, NaCl AND KCl

B. Guo, V. Braun, R.S. Ram, G.A. McRae, K.Q. Zhang and P.F. Bernath

The far infrared emission spectra of gas phase CsI, NaCl and KCl, have been observed using a Bruker IFS 120HR spectrometer. Vibration - rotation emission spectra of CsI near 100 cm^{-1} involving bands from 1 - 0 to 30 - 29 were analyzed. Improved vibrational constants of CsI were derived ($\omega_e = 119.1645(12) \text{ cm}^{-1}$, $\omega_e x_e = 0.250354(93) \text{ cm}^{-1}$, $\omega_e y_e = 0.0002870(19) \text{ cm}^{-1}$). High-resolution vibration-rotational data of KCl and NaCl will also be presented along with the Dunham constants.

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Address of McRae: Laser Science and Applications, AECL Research, Chalk River Laboratories, Chalk River, Ontario, Canada, K0J 1J0.

RH15 15 min 5:04

**TIME RESOLUTION AND FOURIER TRANSFORM SPECTROSCOPY,
G. DURRY, G. GUELACHVILI**

High information time-resolved spectra from a stepping-mode Connes-type Fourier interferometer have been recorded in order to test the main limitations of the method^{1,2}. They show a two-fold improvement on both the time resolution (100 ps) and the total number (10^7) of recorded samples.

Doppler-limited spectra of the N_2 electronic transition $B^3\Sigma - A^3\Pi$, emitted from a microwave excited plasma, over a range of 7000 cm^{-1} are presented with a time resolution of $3\text{ }\mu\text{s}$ as an illustration of these new possibilities in wideband time-resolved spectroscopy.

-
1. G. Durry, G. Guelachvili, D. Mathieu, A. Ubelmann, in 9th International Conference on Fourier Transform Spectroscopy, John E. Bertie, Hal Wieser, Editors, Proc. SPIE 2089, 110-113, (1993)
 2. G. Durry, Thèse de Doctorat, Orsay (1994).

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RH16 15 min 5:21

**USE OF A FOURIER TRANSFORM SPECTROMETER TO STUDY
ION FORMATION MECHANISMS IN A GLOW DISCHARGE**

X. HONG AND TERRY A. MILLER

We have observed with a Bruker 120 Fourier transform spectrometer the Ar^+ emissions from the positive column of a glow discharge in a $Ar/He(1/100)$ mixture. It was found that the Ar^+ emission lines exhibit two distinct Doppler shifts (one an order of magnitude greater than the other), which we characterize as "large" and "small". Experimentally, the emissions from levels with energies $E < E^*$ ($E^* = 159850.3\text{ cm}^{-1}$, the excitation energy of 2^3S He) have "large" Doppler shifts while those with $E > E^*$ have "small" ones. Our analysis leads one to believe that the emissions with "large" Doppler shifts result from excitation of ground state Ar^+ via the reaction $He(2^3S) + Ar^+(3p^5\text{ }^2P_{3/2})$, while the emissions with "small" shifts arise from Ar^+ levels excited directly by electron impact on neutral Ar .

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FA01 15 min 8:30

HYPERFINE QUANTUM BEATS IN C_2N_2 , N. HEMMI, J. VELAZQUEZ, AND T. A. COOL

Molecular quantum beats are observed in the isotropic fluorescence decay following laser excitation of individual rotational states of C_2N_2 via the vibronically allowed $4_0^1 A'(\Sigma_u^+) \leftarrow X(1\Sigma_g^+)$ transition near 219 nm. Strong quantum beats occur with selective excitation, by both P and R branch transitions, of over a dozen rotational states. Observations of hyperfine quantum beats following excitation of the $N'=12$ rotational level yield estimates of spin-orbit coupling matrix elements, Born-Oppenheimer state separations, and magnetic and quadrupolar hyperfine coupling constants. Observations of Zeeman splitting establish that the three hyperfine levels of $N'=12$ are coupled to those of a single triplet state.

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FA02 15 min 8:47

**O_2 SCHUMANN-RUNGE BAND ABSORPTION OF A STRUCTURED SOLAR SPECTRUM,
D. L. HUESTIS AND T. G. SLANGER**

O_2 absorbs solar radiation at wavelengths shorter than 242 nm, leading to photodissociation and formation of ozone. In the wavelength range 174-205 nm the O_2 absorption spectrum consists of relatively sharp peaks, corresponding to transitions to predissociated rovibrational levels of the $B^3\Sigma_u^-$ [the Schumann-Runge (SR) Bands], and relatively deep valleys. Typical widths of the peaks are on the order of 1 cm^{-1} (0.004 nm), while the valleys may be $5\text{-}40\text{ cm}^{-1}$ wide. The complexity and rapid variation of the O_2 absorption spectrum has prompted a number of studies to determine the absorption cross section and to model the resulting atmospheric absorption.

Except near 122 nm, atmospheric modelers largely have assumed that the solar spectrum is relatively smooth and representable by averages over 500 cm^{-1} intervals. In fact, the solar spectrum is strongly structured. In the 174-205 nm range only relatively low resolution (0.007 nm or worse) spectra are available, and thus the "true" intensities of strong features and the underlying background relatively are uncertain. Modulations of $\pm 50\%$ are typical in 0.02 nm . A particularly striking case is provided by three Si^+ lines at 180.80, 181.69, and 181.75 nm, that have intensities at least 20-30 times the mean (perhaps even more, due to limited spectral resolution). The two lines near 181.7 nm overlap three of the rotational lines near the head of the O_2 10-0 SR band.

We have modeled atmospheric absorption in the Schumann-Runge bands using the best available solar data. We find that the 10-0 band is more important than anticipated in ozone production and that the ozone is produced at higher altitudes. Overall, the altitude dependence of ozone formation is surprisingly insensitive to the fine details of the solar spectrum, at least at the available resolution.

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FA03 15 min 9:04

FOURIER TRANSFORM SPECTROSCOPY OF THE HERZBERG I BANDS OF O₂, K. YOSHINO, J.E. MURRAY, J.R. ESMOND, W.H. PARKINSON, A.P. THORNE, AND G. COX

Fourier transform (FT) spectroscopic measurements of the absorption bands of the Herzberg I system ($A^3\Sigma_u^+ - X^3\Sigma_g^-$) of O₂ have been made in the wavelength region 240–270 nm. The FT spectrometer at Imperial College, London is combined with a White cell, that provides a pathlength of 82-m with 16 round trips. The (4,0) through (11,0) absorption bands have been observed and their rotational line positions are determined with an accuracy of $\pm 0.005 \text{ cm}^{-1}$. A weak perturbation is noticed in the F₃ component of the (7,0) band by interaction with the c(12) level. Perturbations are also seen in the (11,0) band as have been noticed previously by Herzberg¹ and Borrell *et al.*². Molecular constants of the A–X system will be presented.

This work is supported by NSF Division of Atmospheric Sciences grants ATM-91-16552 to Harvard College Observatory.

1. G. Herzberg, Can. J. Phys. **30**, 185 (1952).
2. P.M. Borrell, P. Borrell, and D.A. Ramsay, Can. J. Phys. **64**, 721 (1986).

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FA04 15 min 9:21

LIFETIME MEASUREMENTS OF EXCITED STATES IN H₂, M. RAY
AND G. LAFYATIS

We have measured the lifetimes of several rotational-vibrational levels of triplet $n = 3$ gerade states in molecular hydrogen. A plasma discharge creates an intense beam of metastable $2p \text{ } c^3\Pi_u$ levels. From these levels, we populate a specific rotational-vibrational level of an $n = 3$ electronic state by a resonant laser. After a delay, the remaining population is photoionized by a second laser excitation. By measuring the photoionization yield as a function of the delay between the excitation and photoionization lasers, we are able to measure the lifetime of the excited level. We compare our lifetime measurements with recent theoretical results.

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FA05 15 min 9:38

CRITERIA FOR COMPUTER-ASSISTED ASSIGNMENTS IN HYDROGEN EMISSION SPECTRA

Andreas F. Ruckstuhl and Kurt Dressler

Using Dieke's unpublished table of T_2 emission wavelengths we have made new assignments with the aid of a computer-assisted method which is an extension of the one previously described by Loomis and Wood (1928), Rao and coworkers (1969), Nakagawa and Overend (1974), and Winnewisser et al. (J. Mol. Spectrosc. **136**, 12, 1989).

In our search for transitions involving the well-known $B^1\Sigma_u^+$ vibration-rotation levels of T_2 as lower states we have exploited the availability of *ab initio* predictions of the higher singlet *gerade* states of T_2 (Yu and Dressler, unpublished). The calculated term values are generally saddled with systematic deviations from the 'true' ones up to a few cm^{-1} . We have developed an objective procedure to assign spectral lines and to estimate new upper term values. For each predicted upper term we simultaneously consider all expected emission lines. These are now first assigned to those measured lines whose wave numbers lie closest to the corresponding predicted ones and the variability of the resulting set of wave number differences is determined. Next we vary the predicted upper term value and search for minima in the resulting variabilities. To avoid unwanted large contributions to the variability stemming from gaps in the set of measurements we employ methods of robust statistics. The final choice is made considering the systematic variation of $\Delta E(\text{obs-calc})$ with rotational quantum number and expected intensity distributions. Results on the $GK^1\Sigma_g^+$ state of T_2 serve to illustrate the method.

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INTERMISSION

FA06 15 min 10:15

FLUORESCENCE SPECTROSCOPY OF ALKALI ATOMS AND ALKALI CLUSTERS ATTACHED TO LARGE LIQUID HELIUM CLUSTERS

F. Stienkemeier, J. Higgins and G. Scoles

We have built a new apparatus in which laser induced fluorescence (LIF) of atoms, molecules and clusters attached to rare gas clusters can be carried out. The cluster beam source can be operated from room T down to about 10K while the clusters can be seeded with the chromophore of interest in a pick-up cell located immediately after the skimmer. An efficient LIF detector is located a few centimeters downstream of the pick-up point. In the first week of operation, preliminary data have been collected on the $A \leftarrow X$ spectrum of Na_2 attached to large liquid He_n ($n \approx 10^4$) clusters.

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The financial support of the US Air Force under contract #FO 4611-91K0001 is gratefully acknowledged. It is also a pleasure to thank Prof. W. Ernst for useful discussions on the spectroscopy of alkali-clusters.

FA07 10 min 10:32
LASERSPECTROSCOPY OF THE $A \leftarrow X$ TRANSITION OF LiAr

 R. Brühl, D. Zimmermann

Li-Ar molecules have been produced in a supersonic beam by expanding a mixture of Ar gas and Li vapor through a nozzle into a vacuum. A temperature of about 800°C is required in the stagnation area in order to get a sufficient amount of Li atoms in the gas phase. The high-resolution absorption spectrum of the $A^2\Pi \leftarrow X^2\Sigma$ transition of LiAr has been measured between 14720 and 14895 cm^{-1} by scanning a cw dye laser and by observing the laser-induced fluorescence light. Rovibrational quantum numbers could successfully be assigned to about 750 molecular absorption lines of the isotopomer $^7\text{LiAr}$ and to about 120 lines of $^6\text{LiAr}$. The parameters of molecular rotation, of spin-orbit interaction and of λ -type doubling have, up to now, been obtained for vibrational levels $v'' = 0 \dots 2$ of $X\Sigma$ and for $v' = 5 \dots 8$ of $A\Pi$. The molecular spin-orbit interaction of the $A\Pi$ state is about 10 times larger than the spin-orbit splitting of the 2^2P state of the Li atom. Preliminary values of equilibrium distance and well-depth are: 4.87(1) Å, 41(2) cm^{-1} for $X\Sigma$ and 2.49(5) Å, 900(80) cm^{-1} for $A\Pi$.

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FA08 15 min 10:44
DETERMINATION OF THE K-Ar INTERACTION POTENTIAL FOR THE $X\Sigma$ AND $A\Pi$ STATE FROM LASERSPECTROSCOPIC DATA

 F. Bokelmann, D. Zimmermann

The interatomic potential of the K-Ar system has been determined for the molecular states $X^2\Sigma$ and $A^2\Pi$ from laserspectroscopic data using a fully quantum-mechanical approach and using the same analytical functions for the potential as in previous cases [1]. For the first time, we were able to take approximately into account the $B^2\Sigma$ state which due to an avoided crossing lowers the energy values of the upper vibrational levels of the $A^2\Pi_{1/2}$ state. Our experimental data have been derived from a high-resolution absorption spectrum due to the transition $A\Pi \leftarrow X\Sigma$. They consist of rovibrational energy values for $v'' = 0 \dots 3$ of $X\Sigma$ and $v' = 6 \dots 11$ for $A^2\Pi$. The molecular energy levels could accurately be referred to the atomic energy scale by observation of the onset of predissociation in the $A^2\Pi_{3/2}$ state. In addition, the spectral distribution of the fluorescence light $A\Pi \rightarrow X\Sigma$ has been recorded providing information on the repulsive part of the $X\Sigma$ potential. We obtain agreement with all experimental data by using a Tang-Toennies function for $A^2\Pi$, a HFD function for $X^2\Sigma$, and a (12,6) Lennard-Jones potential for $B^2\Sigma$. Our results for equilibrium distance R_e and well-depth D_e are

	$X\Sigma$	$A\Pi_{1/2}$	$A\Pi_{3/2}$	$B\Sigma$
R_e [Å]	5.404(5)	3.37(3)	3.34(3)	7.1
D_e [cm^{-1}]	39.9(5)	405(15)	427(15)	23

[1] R. Brühl et al.: J. Chem. Phys. **94** (1991) 5865 and J. Mol. Spectr. **155** (1992) 277

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FA09 15 min 11:01

**HIGH ROVIBRATIONAL LEVELS IN THE $A^1\Sigma_u^+$ AND $F^1\Sigma_g^+$ STATES OF $^7\text{Li}_2$,
K. URBANSKI, A. YIANNPOULOU, A.M. LYYRA, AND LI LI.**

High rovibrational levels in the $A^1\Sigma_u^+$ have been observed by cw triple resonance spectroscopy. Population was moved to the $F^1\Sigma_g^+$ state via $X^1\Sigma_g^+ \rightarrow A^1\Sigma_u^+ \rightarrow F^1\Sigma_g^+$ which employed two ring dye lasers. A Ti-Sapphire ring laser then dumped population back to higher levels in the $A^1\Sigma_u^+$ state. These levels were detected as dips in the collision induced side fluorescence, $2^3\Pi_g \rightarrow a^3\Sigma_u^+$, which was monitored using a filtered PMT.

High levels in the $F^1\Sigma_g^+$ state have been observed using optical optical double resonance (OODR). Rovibrational levels have been observed up to and beyond the shelf in this state using a filtered PMT and an ionization detector.

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FA10 15 min 11:18

DETERMINATION OF THE LONG RANGE POTENTIAL AND DISSOCIATION ENERGY OF THE Na_2 $1^3\Delta_g$ STATE, B. JI, C.-C. TSAI, LI LI, T.-J. WHANG, H. WANG, A. M. LYYRA, J. T. BAHNS, AND W. C. STWALLEY

Extensive studies on the Na_2 $1^3\Delta_g$ state from $v=0$ up to $v=94$ by Perturbation Facilitated Optical-Optical Double Resonance spectroscopy with an Ultrasensitive Ion Detector¹ has allowed the accurate determination of the long range potential and the dissociation energy. This gives an improved value of D_0 as $7096.56 \pm 0.03 \text{ cm}^{-1}$. Such high resolution spectroscopy also reveals the hyperfine structures at various rotational quantum numbers ranging from $N=2$ to $N=51$.

¹. C.-C. Tsai, J. T. Bahns, and W. C. Stwalley, Rev. Sci. Instrum. **63**, 5576(1992).

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Address of Li Li: Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China.

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FA11 10 min 11:35

LIGHT COLLECTION OPTICS FOR EMISSION SPECTROSCOPY ON THE BRUKER IFS 120 HR SPECTROMETER

P. E. FLEMING, K. I. MAHONEY AND C. W. MATHEWS

Two external optical systems have been designed for efficient light collection for a Bruker IFS 120 HR Fourier transform spectrometer. The systems allow for use of the instrument in multiple experiments by employing kinematically mounted mirrors for beam direction. The systems also maintain maximum flexibility over the wavelength coverage of the instrument while introducing a minimum of geometrical aberrations. The design and implementation of these optics will be discussed.

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FA12 10 min 11:47

REANALYSIS OF VIBRATIONAL RESONANCES IN $\text{SiH}_2 \tilde{X}^1A_1$

H. ISHIKAWA AND O. KAJIMOTO

We have reanalysed the vibrational structure of $\text{SiH}_2 \tilde{X}^1A_1$. In the previous study¹, we found the following three groups of $1\nu_1-2\nu_2$ Fermi resonances, $(1,0,0)-(0,2,0)$, $(1,1,0)-(0,3,0)$, $(2,0,0)-(1,2,0)-(0,4,0)$. In addition, we found a $2\nu_1-2\nu_3$ Darling-Dennison (D-D) resonance between the $(2,0,0)$ and $(0,0,2)$ levels. In our previous analysis, the D-D resonance was ignored and 5 vibrational constants, ω_1^0 , x_{11} , ω_2^0 , x_{22} , x_{12} , and the Fermi interaction energy, $W_{020,100}$ were obtained. One problem was that our value of x_{11} was positive. We considered that the reason for the positive value of x_{11} is our neglect of the D-D resonance. In this study, taking the D-D resonance into account, the following *preliminary* constants (cm^{-1}) were obtained:

$$\begin{aligned} \omega_1^0 &= 2004.00, \quad x_{11} = -11.46, \quad \omega_2^0 = 1002.19, \quad x_{22} = -3.165, \quad x_{12} = -18.04, \\ E_{002}^0 &= 3936.69, \quad |W_{020-100}| = 13.456, \quad |W_{D-D}| = 31.61. \end{aligned}$$

This D-D resonance energy between the $(2,0,0)$ and the $(0,0,2)$ levels is comparable to the Fermi resonance energy between the $(0,4,0)$ and $(1,2,0)$ levels. It was confirmed that the previous positive value of x_{11} was due to the neglect of the D-D resonance. Details of the analysis will be presented.

1. H. Ishikawa and O. Kajimoto, J. Mol. Spectrosc. **150**, 610 (1991), *ibid.* **160**, 1 (1993).

Address of Ishikawa : Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139.

Address of Kajimoto : Department of Chemistry, Kyoto University, Kyoto, Japan, 606-01.

FA13 15 min 11:59**Characterization of the Interacting $(1)^3\Pi_g$ and $(2)^3\Pi_g$ States of the B_2 Molecule**C.R. Brazier and P.G. Carrick

An extensive series of bands connecting the $(1)^3\Pi_g$ and $(2)^3\Pi_g$ states with the $A^3\Pi_u$ state of the B_2 molecule have been observed in emission from a Corona Excited Supersonic Expansion of dilute diborane in helium. The $(2)^3\Pi_g$ - $A^3\Pi_u$ system was recorded at Doppler limited resolution with the 1m Fourier transform spectrometer at Kitt Peak National Observatory. The weaker $(1)^3\Pi_g$ - $A^3\Pi_u$ spectra were recorded at 1 cm^{-1} resolution with a 1.3m monochromator and optical multichannel analyzer. The $(1)^3\Pi_g$ and $(2)^3\Pi_g$ states have an avoided crossing and interact strongly. The $v=0$ level of $(2)^3\Pi_g$ is perturbed by $v=7$ of $(1)^3\Pi_g$, while the $v=1$ level is perturbed by $v=9$. The observation of emission from levels up to $v=9$ in $(1)^3\Pi_g$ has made possible the calculation of potential curves for the two states and a full deperturbation of the interacting vibrational levels. The results of this analysis will be presented.

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FA14 10 min 12:16**Fourier Transform Emission Spectrum of the Triplet System of BH**C.R. Brazier

The $b^3\Sigma^- - a^3\Pi$ system of BH has been observed in emission from a Corona Excited Supersonic Expansion of dilute diborane in helium. The spectrum was recorded at Doppler limited resolution with the 1m Fourier transform spectrometer at Kitt Peak National Observatory. The new spectra provide much improved line positions and molecular constants. The 0-0, 1-1 and 2-2 bands have been analyzed based on the high resolution data. The much weaker off-diagonal bands were recorded at 1 cm^{-1} resolution using a monochromator and OMA. Molecular constants and RKR potential curves will be presented.

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FA15

5 min

12:28

OXYGEN OPTICAL TRANSITION IN COLLISION COMPLEX WITH CHLORINE ATOM

Vitalina V. Kukueva, Boris F. Minaev

The quantum-chemical calculation by method MINDO/3 CI for models of collision complex of oxygen molecule with chlorine atom had been performed. The intermolecular distance (R) is changed from 3,4 Å to 2,8 Å under the symmetrical geometry of rapprochement (C_{2v}) as well as under asymmetrical (C_s).

It is shown, that under the asymmetrical rapprochement the intensity of transition $^1\Delta_g - X^3\Sigma_g^-$ in oxygen is enhanced into seven orders. In an isolated molecule O_2 this transition is magnetic-dipole ($f=4\cdot 10^{-12}$) and induced by spin-orbit coupling (SOC); and in collision complex with chlorine it acquires electric-dipole character (without account of SOC) by some charge-transfer-state admixtures $O_2^+ - Cl^-$.

It is interesting to note that the $^1\Delta_g - X^3\Sigma_g^-$ transition intensity in oxygen under the geometry of rapprochement C_s ($f=1,2\cdot 10^{-5}$) enhances in three orders the intensity of the same transition but under symmetry C_{2v} ($f=7,4\cdot 10^{-8}$). Moreover the radiative lifetime of oxygen molecule metastable state $^1\Delta_g$ in the symmetry C_{2v} ($\tau=0,63$ s) exceeds in 63 times the radiative lifetime than the C_s configuration.

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FB01 15 min 8:30

THE VIBRATIONAL ENERGY PATTERN IN ACETYLENE I
M. ABBOUTI TEMSAMANI, Q. KOU, G. GUELACHVILI, A. PISARCHIK,
A. HELD AND M. HERMAN

Energy, and mainly relative intensity information from high resolution absorption spectra recorded over a very broad energy range are used to point out anharmonic couplings in various isotopomers of acetylene, C_2H_2 , C_2HD and C_2D_2 . Some of them are reported for the first time. They will be exemplified in particular from new experimental data around $1.5 \mu m$, in C_2H_2 .

In addition, the results of FTIR resolved-LIF experiments will be reported, if successful by the time of the meeting.

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FB02 10 min 8:47

THE VIBRATIONAL ENERGY PATTERN IN ACETYLENE II
M. ABBOUTI TEMSAMANI AND M. HERMAN

All vibrational levels reported in the literature for acetylene will be gathered in simultaneous fitting procedures, for C_2HD on one hand and for C_2H_2 on the other hand. We shall focus on the main isotopomer. The clustering of the vibrational levels will be discussed.

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FB03 15 min 8:59

**INTRAMOLECULAR VIBRATIONAL REDISTRIBUTION IN SEVERAL
OVERTONE BANDS OF DIACETYLENE AND DIACETYLENE-D₁**

J. E. Gambogi, R. Z. Pearson, X. Yang, K. K. Lehmann, and G. Scoles

We have recorded the high resolution spectrum of several overtone bands in diacetylene and diacetylene-d₁ using optothermal detection of a collimated molecular beam. The first overtones of the acetylenic CH stretches in these two molecules were recorded by single resonance using a 1.5 μm color center laser. The second overtone spectra were taken using sequential infrared/infrared double resonance with two color center lasers. In diacetylene we also recorded a combination band, which in the local mode picture is equivalent to putting two quanta in one acetylenic CH stretch and one quanta at the other end of the molecule. Comparison of this spectrum with the spectrum of three quanta in the same CH stretch confirms earlier observations that, if the molecule is not too small, "extreme motion" states are more perturbed than combination bands¹. The interesting and varied dynamics found in these two linear molecules cannot be attributed to such things as exciting different types of bonds, internal rotation or isomerization, but instead comes purely from the anharmonic couplings present in each molecule.

¹J. E. Gambogi, J. H. Timmermans, K. K. Lehmann, and G. Scoles, *J. Chem. Phys.*, **99**, 9314 (1993).

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FB04 15 min 9:16

PRECISION MEASUREMENTS OF ACETYLENE SPECTRA AT 1.4-1.7 μm RECORDED WITH 16-352m PATHLENGTH

KAREN A. KEPPLER, K. NARAHARI RAO, JOSEF PLÍVA, STEFAN KLEE, GEORG MELLAU, BRENDA P. WINNEWISSER, AND MANFRED WINNEWISSER.

The spectrum of acetylene between 5700-7100 cm^{-1} has been measured at pressure-broadening-limited resolution at room temperature with a Bruker FTS 120HR and a White-type cell adjusted to provide pathlengths of 16-352m. Sample pressures used were 0.075-50 mbar. Spectral line positions were determined relative to the 3-0 band of CO, known to an accuracy better than 0.0001 cm^{-1} . Over 30 bands of $^{12}\text{C}_2\text{H}_2$ and $^{13}\text{C}^{12}\text{CH}_2$ have been identified. Perturbations have been taken into account in the analysis. The molecular parameters determined considerably improve our knowledge of the spectrum ^a. The current interest of acetylene studies in this spectral region is evident from the information available in the report of Kou, et al. ^b, and the recent photoacoustic measurements of Demtröder, et al. ^c. The present study includes regions not covered by Guelachvili and Rao ^d. The spectrum will be presented and the results discussed.

^aA. Baldacci, S. Ghersetti and K. Narahari Rao, *J. Mol. Spec.*, **68**, 183 (1977); B. C. Smith and J. S. Winn, *J. Chem. Phys.*, **89**, 4638, (1988), and references quoted within.

^bQ. Kou, G. Guelachvili, M. Abbouuti Tamsamani, and M. Herman, 13th Colloquium on High Resolution Molecular Spectroscopy, Riccione, Italy, Poster J25, September 1993.

^cW. Demtröder, et al., Spring Meeting of the German Physical Society, Hamburg, Germany, March 1994.

^dG. Guelachvili and K. Narahari Rao, *Handbook of Infrared Standards II*, Academic Press, San Diego, 1993.

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Address of Plíva: Department of Physics, The Pennsylvania State University, University Park, PA 16802, USA.

FB05

15 min

9:33

MOLECULAR DYNAMICS IN ACETYLENE: EFFECTIVE HAMILTONIAN MODELS AND OPTIMAL INTERMEDIATE STATES FOR DISPERSED FLUORESCENCE SPECTRA, S.A.B. SOLINA, J.P. O'BRIEN, W. POLIK, and R.W. FIELD

From Dispersed Fluorescence (DF) and Stimulated Emission Pumping (SEP) spectra of acetylene, it is now known that the only Franck-Condon active modes for the $\tilde{A} \leftrightarrow \tilde{X}$ transition are the CC stretch (ν_2) and the *trans*-bend (ν_3). Energy placed into these zero order modes flows via Intramolecular Vibrational Redistribution (IVR), first into *cis*-bend (ν_3), due to Darling-Dennison (DD) resonances; then, for initial states with CC stretch excited, into states containing at least one quantum of *anti*-symmetric CH stretch due to the "2345" anharmonic resonance.^{1,2} From a naive "ball and spring" model of acetylene, selective excitation in these modes is a plausible scheme for promoting the unimolecular isomerization of acetylene to vinylidene. To further elucidate the dynamics of acetylene, we have been using a superpolyad effective Hamiltonian, developed from the previous SEP studies recorded at 7000 cm⁻¹, to model the fractionation patterns of the zero-order states. High quality dispersed fluorescence spectra of acetylene have been recorded utilizing the zero-point vibrational level of the \tilde{A} state. These DF spectra reveal Franck-Condon bright feature states and their early time dynamics as each bright state evolves in its own separate superpolyad. Each superpolyad is labeled by three good quantum numbers $n_{\text{resonance}}$, n_{stretch} , and l_{total} . The qualitative intensity and energy splitting patterns observed in each superpolyad permit refinement of the molecular constants, especially the resonance strength parameters. Proper scaling behavior from one superpolyad to the next provides a stringent test of the multi-resonance model.

1. K. Yamanouchi, N. Ikeda, S. Tsuchiya, D.M. Jonas, J.K. Lundberg, G.W. Adamson, and R.W. Field, *J. Chem. Phys.* **95**(9), 6330-6342 (1991).

2. D.M. Jonas, S.A.B. Solina, B. Rajaram, R.W. Field, R.J. Silbey, K. Yamanouchi, and S. Tsuchiya, *J. Chem. Phys.* **99**(10), 7350-7370 (1993).

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FB06

10 min

9:50

THE VIBRATIONAL ENERGY PATTERN IN N₂O

M. BACH, D. HURTMANS, A. HELD, J. VANDER AUWERA AND M. HERMAN

We have recorded the absorption spectrum of nitrous oxide at high resolution with a Fourier transform interferometer, from the mid-infrared to the near-infrared ranges. Several bands are reported for the first time and tentatively assigned in this work. We shall first report on the 1250 cm⁻¹ energy range, taking care of new absolute intensity and line broadening measurements, as well as of an artificial line removal technique. We shall then examine the evolution of the anharmonic couplings in higher energy ranges.

In addition, the results of experiments performed, some in absorption with a laser and some with a new long-slit jet apparatus coupled to the Fourier transform instrument will be reported, if successful by the time of the meeting.

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INTERMISSION

FB07 5 min 10:20

THE VIBRATIONAL ENERGY PATTERN IN N_2O_4
Y. ELYOUSSOUFI, I. KLEINER, M. HERMAN AND J. LIEVIN

We have recorded the absorption spectrum of nitrogen hemitetraoxide at medium resolution with a Fourier transform interferometer, from the mid-infrared to the near-infrared ranges. Several new bands are assigned in this work. The assignment is supported by extended *ab initio* calculations. Special attention is brought to the torsion vibration.

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FB08 15 min 10:26

**REINVESTIGATION OF THE $2\nu_1$ BAND IN TRIFLUOROPROPYNE USING
 INFRARED/INFRARED DOUBLE RESONANCE**

M. Becucci, J. E. Gambogi, K. K. Lehmann, and G. Scoles

The highly perturbed spectrum of the first overtone of the acetylenic CH stretch in trifluoropropyne has been reinvestigated using high resolution infrared/infrared double resonance. The double resonance technique allows for eigenstate-resolved rotational assignments. A resonant build-up cavity was used in conjunction with the overtone laser to increase both the signal level and resolution, in comparison to our previous method of multi-passing the molecular beam with the radiation. Analysis of the spectrum indicates that the lifetime for the acetylenic CH stretch, at this level of excitation, is about 1.4 nsec and does not vary as a function of J' for $J' < 5$. The P(1) clump has an experimental density of states of $1150/\text{cm}^{-1}$ which is almost equal to the calculated density of symmetry allowed states, indicating that many or all modes within the molecule eventually receive the excitation.

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FB09 15 min 10:43

ANALYSIS OF THE $2\nu_3$ BAND OF CF_4 ($2540\text{--}2600\text{ cm}^{-1}$),
A. NIKITIN, T. GABARD, J.P. CHAMPION, G. PIERRE, A.G. ROBIETTE AND A.S. PINE

An analysis of the F_2 and E vibrational components of the $2\nu_3$ band of CF_4 in the infrared between 2540 and 2600 cm^{-1} will be presented. A nearly Doppler-limited spectrum was recorded using a difference-frequency laser with the CF_4 sample contained in a White cell cooled to $T \approx 77\text{ K}$ ($P \approx 8\text{ Pa}$, $L \approx 8\text{ m}$) to reduce spectral congestion. An analysis was performed using an isolated band model to sixth order in the tetrahedral formalism. The $2\nu_3$ assignments were initiated using predictions from a vibrational extrapolation method¹ based on constants of the ν_3 band² and anharmonic force field calculations³ of the $2\nu_3$, $A_1 + E + F_2$ sublevel centers. Only 22 free parameters were adjusted (the ν_3 parameters were held fixed in the analysis). 1475 transitions were assigned through $J=35$, of which 1005 were fit with a standard deviation of 0.0021 cm^{-1} , which is considerably larger than the measurement precision estimated to be $\approx 0.0001\text{ cm}^{-1}$. Some of the discrepancies can be clearly attributed to interactions with the $\nu_3 + 2\nu_4$ and $4\nu_4$ bands as expected from the extrapolation of the $\nu_3/2\nu_4$ band system².

1. J.P. Champion, M. Loete, G. Pierre, Spherical Top Spectra in "The Spectroscopy of the Earth Atmosphere and Interstellar Medium", edited by K.N. Rao and A. Weber, Academic Press, New York (1992).
2. G. Pierre and M. Takami, unpublished results.
3. R.K. Heenan and A.G. Robiette, unpublished results.

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FB10 15 min 11:00

THE HIGH RESOLUTION IR SPECTRUM OF SEVERAL BANDS OF $t\text{-}^{13}\text{CHF}=\text{}^{13}\text{CHF}$: THE MOLECULAR STRUCTURE OF $t\text{-}1,2\text{-DIFLUOROETHYLENE}$.

Norman C. Craig, Oliver P. Abiog, Baonian Hu and W.J. Lafferty

Over the last five years, we have been investigating the high resolution IR spectra of $t\text{-}1,2\text{-difluoroethylene}$ (TDFE) and several isotopic species with the goal of obtaining accurate ground state rotational constants and a complete structure for this nonpolar molecule. In order to completely define the structure without the requirement of structural assumptions, we have synthesized the $^{13}\text{C}_2$ isotopomer, the last species needed to define a structure completely. Two a -type bands (one arising from the C-F stretching vibration; the other from the C-H in plane bending motion), and a c -type band arising from the out-of-plane C-H bending have been studied. Over 800 ground state combination differences have been fit using a standard Watson Hamiltonian. The uncertainties in the rotational constants obtained are equivalent to those typically obtained in microwave studies ($\approx 0.03\text{ MHz}$).

The ground state constants of TDFE- d_0 , TDFE- d_1 , and TDFE- d_2 have been determined and reported previously. With the addition of the data from the ^{13}C isotopomer, the molecular structure can be calculated by a number of methods. Using a "Kraitchman" treatment, which places the H and C atoms, and the second moment constraint, the following structural parameters are obtained:

$r_{\text{CH}} (\text{\AA})$	$r_{\text{C}=\text{C}} (\text{\AA})$	$r_{\text{CF}} (\text{\AA})$	$\angle \text{C}=\text{CH} (^{\circ})$	$\angle \text{C}=\text{CF} (^{\circ})$
1.080	1.318	1.352	126.6	119.1

The parameters obtained differ significantly from those determined for the *cis* isomer by Laurie and Pence¹; e.g. the CCF angle in the *cis* form is 4 degrees larger. The significance of these changes will be discussed.

1. V.W. Laurie and D.T. Pence, J. Chem. Phys. **38**, 2693 (1963).

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FB11 15 min 11:17

FOURIER TRANSFORM SPECTROSCOPY AND FIR LASER EMISSION IN THE CH₃-ROCKING BAND OF C-13 METHANOL, A. PREDOI, LI-HONG XU, R.M. LEES, M. NOEL, AND J.W.C. JOHNS

Fourier transform spectra have been recorded at 0.002 cm⁻¹ resolution for the ¹³CH₃OH isotopomer of methanol in the region from 900-1100 cm⁻¹, covering the strong CO-stretching band and the much weaker in-plane CH₃-rocking band. Analysis of the rocking band has led to the assignment of a number of optically-pumped far-infrared (FIR) laser lines to transitions within this band. As well, further results for FIR laser lines pumped in the CO-stretching band have been obtained. The transition and energy level system identifications have been checked in most case by closed-loop combination difference relations utilizing our infrared data plus FIR spectra of the torsion-rotation subbands in the ground vibrational state. Preliminary analysis of the assigned subbands of the CH₃-rocking fundamental indicates significant change in the torsion-rotation energy level structure compared to the ground state, for which one interpretation is a substantially increased effective barrier height V₃ in the rocking mode.

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FB12 10 min 11:34

Absolute Intensity Measurements in ¹⁶O¹²C³²S: the ν₁ + ν₃ Region

Q. Errera, J. Vander Auwera and A. Fayt

We have measured the absolute intensity of about 400 rotational lines of 6 bands of ¹⁶O¹²C³²S in the region between 2500 and 3200 cm⁻¹. The measurements were made on spectra recorded at a resolution of 0.005 cm⁻¹ using a Bruker IFS120HR spectrometer. Five of the bands exhibit weak to strong Herman-Wallis dependencies.

Experimental details as well as the final results obtained, including transition moments, band strengths and Herman-Wallis corrections, will be presented. These results will be discussed in terms of the interactions between the energy levels observed in this energy range.

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FB13 15 min 11:46
A ROVIBRATIONAL ANALYSIS OF THE ν_2 C-H STRETCHING VIBRATION ENERGY MANIFOLD IN THE LINEAR SPECIES HCN---HF, A.M. GALLEGOS, A.L. McINTOSH, J.W. BEVAN

Previously, the rovibrational spectrum of ν_2 , the C-H stretching vibration in the linear hydrogen-bonded species HCN---HF was analyzed through the use of a frequency color-center laser spectrometer in our laboratory.¹ We now extend our analysis to include a total of twelve hot bands involving ν_2 . These bands include the ν_2 fundamental itself, as well as the hot bands involving ν_2 and each of the following states: $2\nu_7^0$, ν_7^1 , $2\nu_7^2$, $3\nu_7^3$, $3\nu_7^1$, $4\nu_7^0$, $4\nu_7^2$, $4\nu_7^4$, ν_4 , $\nu_4 + \nu_7^1$, and $\nu_4 + 2\nu_7^2$. We report the relevant rovibrational parameters ν_0 , B'' , B' , D'' , and D' for each band, as well as the splitting constants q'' and q' for the doubly degenerate bands.

1. E.K. Kyro, M. Eliades, A.M. Gallegos, P. Shoja-Chagervand, and J.W. Bevan, J. Chem. Phys. **85**, 3 (1986).

Address of Gallegos, McIntosh, and Bevan: Department of Chemistry, Texas A&M University, College Station, TX 77843.

FB14 15 min 12:03
INVESTIGATION OF THE GROUND VIBRATIONAL STATE STRUCTURE OF H^{35}Cl TRIMER BASED ON RESOLVED K, J SUBSTRUCTURE OF THE ν_5 VIBRATIONAL BAND, J. HAN, Z. WANG, A. L. McINTOSH, R. R. LUCCHESI, AND J. W. BEVAN

The high-resolution rovibrational infrared spectrum of the antisymmetric HCl stretching ν_5 vibrational band in the $(\text{H}^{35}\text{Cl})_3$ isotopomer of the trimer has been measured with a tunable infrared diode-laser supersonic-jet spectrometer. This spectrum of $(\text{H}^{35}\text{Cl})_3$ was analyzed as the perpendicular band of an oblate symmetric rovibrator. By fitting 527 rovibrational transitions with root-mean-square error of $\pm 0.00054 \text{ cm}^{-1}$, the following molecular parameters were obtained for the trimer:

$$\begin{aligned} \nu_0 - C'' &= 2809.77698(6) \text{ cm}^{-1}, B'' = 6.80414(55) \times 10^{-2} \text{ cm}^{-1}, B' = 6.85943(55) \times 10^{-2} \text{ cm}^{-1}, \\ C' - C'' &= 2.737(78) \times 10^{-4} \text{ cm}^{-1}, D_{JK}'' = 8.40(38) \times 10^{-7} \text{ cm}^{-1}, D_{JK}' = 8.14(38) \times 10^{-7} \text{ cm}^{-1}, \\ D_J'' &= 4.26(16) \times 10^{-7} \text{ cm}^{-1}, D_J' = 4.16(16) \times 10^{-7} \text{ cm}^{-1}, D_K'' = 4.32(22) \times 10^{-7} \text{ cm}^{-1}, \\ D_K' &= 4.16(22) \times 10^{-7} \text{ cm}^{-1}. \end{aligned}$$

A relationship among the centrifugal distortion constants establishes that the geometry of $(\text{H}^{35}\text{Cl})_3$ is consistent with a dynamically averaged planar ground vibrational state. The centers of mass of the HCl components are separated by $3.693(1) \text{ \AA}$ in this structure. *Ab initio* methods were also used to estimate the splitting due to the tunneling motions between clockwise (cw) and counterclockwise (ccw) identical structures. Both theoretical and experimental evidence indicate that the $(\text{H}^{35}\text{Cl})_3$ complex has a planar equilibrium structure with no observable tunneling probability between the cw and ccw forms, thus the molecular symmetry of the complex is proposed to be $C_{3h}(\text{M})$.

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FB15 15 min 12:20

ROVIBRATIONALLY RESOLVED, CONTINUOUS SUPERSONIC-JET FOURIER TRANSFORM INFRARED ABSORPTION SPECTROSCOPY OF WEAKLY BOUND DIMERS. R. MEADS, C. HARTZ, R. LUCCHESI AND J. BEVAN

Rovibrational analysis of the ν_1 and ν_2 vibrational bands of OC--H³⁵Cl and OC--H³⁷Cl have been carried out using continuous supersonic-jet, Fourier transform, infra-red absorption spectroscopy. The following molecular parameters were determined (in cm⁻¹). For OC--H³⁵Cl: $\nu_1=2851.76061(21)$; $B'_1=0.0560443(31)$; $D'_1=1.795(80) \times 10^{-7}$; $\nu_2=2155.50001(13)$; $B'_2=0.0554824(10)$; $D'_2=1.650(15) \times 10^{-7}$. For OC--H³⁷Cl: $\nu_1=2849.67217(54)$; $B'_1=0.0547611(55)$; $D'_1=1.63(11) \times 10^{-7}$; $\nu_2=2155.50626(62)$; $B'_2=0.0542013(21)$; $D'_2=1.48(16) \times 10^{-7}$. Additionally, rovibrationally resolved spectra of the weakly bound complexes of Ar--HCl, N₂--HCl and (HCl)₂ will also be presented to illustrate the utility that SSJ-FTIR offers to the spectroscopic studies of gas-phase molecular species.

1. R.F. Meads, C.L. Hartz, R.R. Lucchese and J.W. Bevan, Chem Phys. Lett. 206, 488(1993)

Address of R.F. Meads: Department of Chemistry, M.I.T., Cambridge, Massachusetts 02139.

Address of C.L. Hartz, R.R. Lucchese and J.W. Bevan : Department of Chemistry, Texas A&M University, College Station, Texas 77840.

FB16 15 min 12:37

DIODE LASER SPECTROSCOPY IN A N₂ - H₂ - He DISCHARGE: THE ν_4 BAND OF NH₃⁺
FRANK KÜHNEMANN, SANGWOO JOO, AND TAKESHI OKA

The spectrum of the NH₃⁺ ion has already been studied in our group using a Difference Frequency System (ν_3 band¹ and $\nu_2 + \nu_3 - \nu_2$ band²) and the Diode Laser Spectrometer (ν_2 band³). The analysis of these bands was complicated due to the strong Coriolis interaction⁴ between the ν_2 and ν_4 states and a lack of information about the latter.

In our attempt to improve and complete this analysis we present here the first observation of the NH₃⁺ ν_4 band in the region around 7 μm . Spin rotation doublets have been observed with splittings between 0.01 and 0.07 cm⁻¹. The spectra have been measured in air- and liquid nitrogen-cooled ac glow discharges of N₂, H₂ and He using a Tunable Diode Laser Spectrometer. The velocity modulation technique was used to detect the ion signals. Lines of the ν_4 band of NH₄⁺, which also occur in this region, have been discriminated using additional NH₃ - H₂ discharges, which give very strong NH₄⁺ signals.

It is our hope, that the ν_4 band data of NH₃⁺ will allow us also an improvement of the analysis of the ν_2 and $\nu_2+\nu_4-\nu_2$ bands.

¹) M.G.Bawendi, B.D.Reh fuss, B.M.Dinelli, M.Okumura, and T.Oka, J.Chem.Phys. 90, 5910 (1989)

²) T.R.Huet, Y.Kabbadj, C.M.Gabrys, and T.Oka, J.Mol.Spectrosc. 163, 206 (1994)

³) S.S.Lee and T.Oka, J.Chem.Phys. 94, 1698 (1991)

⁴) W.P.Kraemer, V.Spirko, J. Mol. Spectrosc. 153, 276 (1992)

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FB17 10 min 12:54**Discharge modulation technique in a supersonic jet for infrared diode laser absorption spectroscopy**

Takashi Imajo, Keiichi Tanaka, and Takehiko Tanaka.

A new discharge modulation technique for the detection of transient molecules in the supersonic jet has been devised for the infrared diode laser spectroscopy. Comer and Foster¹ have reported a discharge modulation method combined with corona discharge.

Carbon disulfide diluted to 3 % with 4 atm Ar was injected in an absorption cell through a discharge nozzle with a repetition rate of 6 Hz. A cathode, made of 4 mm id tantalum tube and isolated with a teflon plate was attached to a commercial solenoid valve with 2 mm circular orifice. The cathode was surrounded by an anode made of a 50 mm id stainless steel tube. Between the electrodes, 20 kHz ac high voltage pulse was applied for the duration of 1 ms, synchronized with the pulsed jet, to cause stable ac discharge of 100 mA, typically. Focused diode laser beam in a Perry-type multireflection path crossed the molecular jet beam 16 times just below (2~6 mm). As the first test of the nozzle, we observed the R(3) line in the fundamental band of the CS radical in the time as well as frequency domain. The change in the density of CS was clearly observed with 50 μ s repetition corresponding to the 20 kHz rectified discharge current, although CS is almost stable. The CS radical was generated at the throat of the cathode and expanded with the speed of ~500m/s outside of the discharge nozzle to be cooled down to a rotational temperature of a few tens of K. Infrared signal was demodulated by a phase sensitive detector with a time constant of 1 ms and averaged by a boxcar integrator. The present discharge modulation resulted in an improvement of the S/N ratio by 3~4 times.

1. K. R. Comer and S. C. Foster, Chem. Phys. Lett., 202, 216 (1993).

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FC01 15 min 8:30

**THE MICROWAVE SPECTRUM OF THE OPEN-SHELL COMPLEX ArNO_2 ,
R.J. LOW, C.J. WHITHAM, T.D. VARBERG and B.J. HOWARD**

The microwave spectrum of the Ar-NO_2 open-shell complex has been measured for the $K_A=0$ and 2 states using a pulsed Fourier transform spectrometer between 7 and 18 GHz. We are able to study the interaction of the radical with its closed shell partner, which is expected to be intermediate between chemical and physical bonding. Also, the long range coupling of the electronic spin and orbital angular momenta to the intermolecular motion is important in the chemistry of free radicals. The high resolution offered by microwave spectroscopy has allowed us to probe fine, magnetic hyperfine and electric quadrupole interactions found in this system. The $K_A=0$ data has been fitted to a semi-rigid Hamiltonian to determine the molecular parameters for this state, and have been used to derive an effective structure. $K_A = 2$ transitions have also been observed. Full analysis of both these states will be presented, along with the implications the derived parameters have on the electronic and geometric structure of the complex.

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FC02 15 min 8:47

DETERMINATION OF THE STRUCTURE OF HBr OCS

**A.R. HIGHT WALKER, WEI CHEN, STEWART E. NOVICK, BRIAN D. BEAN,
AND MARK D. MARSHALL**

Guided by the infrared spectroscopy of Hu and Sharpe first reported at this meeting last year¹ and by more recent measurements from the same laboratory², we have investigated the structure and dynamics of the weakly bound complex HBr OCS using pulsed-jet Fourier transform microwave spectroscopy. The complex is linear and is not hydrogen bonded. The wide amplitude bending of the HBr results in a effective angle of 26° between the H-Br bond and the O-C-S-Br line. Approximate values for the spectroscopic constants of the $\text{O=C=S} - ^{81}\text{Br-H}$ isotopomer are: $B = 484.050$ MHz, $D_J = 2.7$ kHz, and $\chi_{\text{ea}} = +310.3$ MHz. In order to fit the spectrum it is necessary to include a term in the Hamiltonian which allows for centrifugal distortion of the Br quadrupole coupling constant, χ_{ea} .

-
1. T.A. Hu and S.W. Sharpe, 48th Symposium on Molecular Spectroscopy, Columbus, Ohio, paper WG03 (1993).
 2. S.W. Sharpe, private communication.

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FC03 15 min 9:04

DIPOLE MOMENT OF THE LOWEST Π BENDING STATE OF $(\text{HCN})_2$

A. Grushow, W.A. Burns, and K.R. Leopold

The dipole moment of the lowest Π bending state of $(\text{HCN})_2$ has been measured by tunable far infrared difference frequency spectroscopy in a supersonic jet. Stark effect measurements of the R(1) transition were made at electric field strengths up to 110 V/cm, and the Stark shifts used to determine the dipole moment. The ℓ -type doubling constant is crucial to an accurate determination of the dipole moment, and hence was remeasured from zero field spectra with improved accuracy over previous work. The zero field and Stark effect data were combined to obtain a value of 6.02(7) D for the dipole moment of the excited bending state, indicating a reduction of 0.54(9) D from the ground state value.

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FC04 15 min 9:21

PROTON INTERCHANGE TUNNELING AND FREE INTERNAL ROTATION IN $\text{H}_3\text{N--HSH}$

G. Hilpert, E.N. Karyakin, G.T. Fraser, and R.D. Suenram

An electric-resonance optothermal spectrometer and phase-locked backward-wave oscillators are used to investigate the b -type, $\Delta K=1$, $\Delta m=0$ spectrum of $\text{H}_3\text{N--HSH}$ and $\text{H}_3\text{N--H}^{24}\text{SH}$ near 300 GHz. The spectrum is characterized by nearly free internal rotation of the NH_3 against the H_2S , as initially concluded from Stark-effect measurements by Herbine *et al.*¹. Transitions are observed for the $K = 1 \leftarrow 0$, $m = 0$, A symmetry and the $K = 0 \leftarrow 1$ and $2 \leftarrow 1$, $m = \pm 1$, $K_m > 0$, E-symmetry subbands. The transitions are split into doublets with a 3:1 relative intensity ratio indicative of interchange tunneling of the two H_2S protons. From the observed selection rules, symmetric \longleftrightarrow antisymmetric in the tunneling state, it follows that the tunneling pathway must reverse the sign of the μ_b component of the molecular electric dipole moment. The most likely interchange motion consists of a partial internal rotation of the H_2S unit about its c inertial axis, through a bifurcated, doubly hydrogen-bonded transition state. The proton interchange tunneling splittings range from 859 - 864 MHz, indicating that the interchange motion is only weakly coupled to the internal rotation. The barrier to proton interchange is calculated to be 510(3) cm^{-1} which can be compared to the $\sim 700 \text{ cm}^{-1}$ barrier determined from the 57 MHz tunneling splittings associated with H_2O proton interchange in the related $\text{H}_3\text{N--HOH}$ complex².

¹ P. Herbine, T.A. Hu, G. Johnson, and T.R. Dyke, *J. Chem. Phys.* **93**, 5485 (1990).

² P.A. Stockman, R.E. Bumgarner, S. Suzuki, and G.A. Blake, *J. Chem. Phys.* **96**, 2496 (1992).

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FC05 10 min 9:38

Infrared Spectroscopy of the C-O Stretching Band in Methanol/Acetone Dimer

W. D. Stork, C. T. Laush, and J. M. Lisy

Molecular Beam Depletion Spectroscopy (MBDS) has been used to record the C-O stretching band of both $\text{CH}_3\text{OH} / (\text{CH}_3)_2\text{CO}$ and $\text{CH}_3\text{OD} / (\text{CH}_3)_2\text{CO}$. In each dimer, the hydroxy H/D of the methanol is hydrogen bonded to the oxygen of the acetone. Upon electron impact ionization and H/D transfer, the resulting protonated acetone ion is selected for detection by an off-axis quadrupole. A line tunable CO_2 laser operating in the 9.6μ P-branch region is used to dissociate the dimers.

Spectral results for these mixed dimers will be presented and compared with earlier observations of the C-O stretching bands of $(\text{CH}_3\text{OH})_2^1$ and $(\text{CH}_3\text{OD})_2^2$

¹ Huiskens, F., Stemmler, M., *Chem. Phys. Lett.*, **1988**, 144(4), 391.

² LaCrosse, J. P., Lisy, J. M., *J. Phys. Chem.*, **1990**, 94, 4398

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FC06 15 min 9:50

GLOBAL FIT OF TUNNELING SPLITTINGS IN THE K=0 A-TYPE MICROWAVE SPECTRUM OF THE METHANOL DIMER **NOBUKIMI OHASHI AND JON T. HOUGEN**

Theoretical results previously developed using an IAM-like multi-dimensional tunneling formalism are applied to tunneling splitting patterns recently measured at NIST and Kiel University for a-type R(J) microwave transitions for various isotopomers of the methanol dimer. Permutation-inversion group G_{36} species assignments for the 16 tunneling components of a given R(J) transition arising from 25 different tunneling motions are presented for $0 \leq J \leq 4$ for the normal isotopomer. Permutation-inversion group G_{18} species assignments for the 10 tunneling components of a given R(J) transition arising from 13 different tunneling motions are presented for $0 \leq J \leq 3$ for the two mixed $^{12}\text{C}, ^{13}\text{C}$ isotopomers. As a first stage of the analysis, a simplified two-top treatment of suitably averaged line frequencies is carried out in which only the (dominant) tunneling splittings arising from internal rotation of the two methyl tops of the dimer is considered. Relatively large top-top interaction terms must be included in this two-top treatment, which is surprising in view of the large distance between the two methyl rotors in the methanol dimer. As a second stage of the analysis, a tunneling treatment taking into account all tunneling splittings is carried out. Because only K=0 a-type transitions are available, some ambiguity remains in the symmetry assignments and tunneling parameters reported in this work.

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INTERMISSION

FC07 15 min 10:30

Patterns of Orientational Order in Polar Clusters

Holly B. Lavender, Karthik A. Iyer and Sherwin J. Singer

Department of Chemistry, Ohio State University

Patterns of orientational order in polar clusters arise from the tendency of dipolar particles to form chains in which the dipoles are in a head-to-tail configuration. These chains encircle the cluster leading to a pronounced circulating pattern. The circulating pattern is quite evident in minimum energy configurations of polar clusters, and is distinct from orientational order in dipolar solids (much as the icosahedral translational order of rare gas clusters is distinct from the close packed structure of rare gas solids). Orientational order is surprisingly persistent at elevated temperatures in the model 13-particle cluster with Stockmayer interactions (Lennard-Jones + point dipoles) examined in our work. Quantified by an appropriate order parameter, we even detect the circulating pattern *above* the translational melting point.

FC08 10 min 10:47

DETECTION OF NON-RADIATIVE RELAXATION CHANNELS IN ELECTRONICALLY EXCITED MOLECULES USING OPTOTHERMAL DETECTION

C. Cameron Miller, Kevin B. Hewett and Laura A. Philips

Optothermal detection has been used to observe non-radiative relaxation channels in aniline, *p*-bromoaniline and *trans*-stilbene. A comparison of aniline and *p*-bromoaniline exemplifies the power of this technique. *p*-Bromoaniline has no detectable fluorescence due to a heavy atom effect which increases the rate of intersystem crossing to the triplet state. An optothermal detection spectrum of *p*-bromoaniline was observed with the origin at 32625 cm⁻¹. For *trans*-stilbene the differences between the laser excitation spectrum and the optothermal detection spectrum of the S₁ state clearly show the onset of isomerization at 1100-1200 cm⁻¹ above the origin. Relative quantum yields of fluorescence and Franck-Condon factors have been obtained for a series of vibronic transitions. For low energy vibrational states there is good agreement between the current study and previous work. For vibrational energies above the barrier of isomerization the predicted relative quantum yields do not agree with our experimental results. Our results show that the Franck-Condon factors are more important in the loss of fluorescence intensity than previously reported.

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FC09 15 min 10:59

HIGH RESOLUTION INFRARED SPECTROSCOPY OF PYRAZINE AND NAPHTHALENE IN A MOLECULAR BEAM

Kevin B. Hewett, Meihua Shen, Christopher L. Brummel and Laura A. Philips

The high resolution infrared spectrum of pyrazine and naphthalene were measured in a molecular beam in the vicinity of the C-H stretching transitions. In the case of pyrazine, two vibrational bands were examined, the ν_9 band from 3015-3019 cm^{-1} and the ν_{15} band from 3065-3073 cm^{-1} . The rotational structure in the ν_9 band is well modeled by an asymmetric top/rigid rotor Hamiltonian with no significant perturbations. The rotational structure in the ν_{15} band reveals that this C-H stretch is coupled to one other vibrational mode in the molecule. The mode coupling is manifested in the spectrum as two overlapping vibrational bands. Each of these two bands are well modeled by an asymmetric top/rigid rotor Hamiltonian. The lack of any angular momentum dependence on the coupling indicates that the vibrations are coupled by an anharmonic mechanism. The magnitude of the coupling matrix element was determined to be 0.36 cm^{-1} . The rotational structure in the spectrum of naphthalene from 3063-3067 cm^{-1} reveals that except for several local perturbations, the spectrum is well modeled by an asymmetric top/rigid rotor Hamiltonian. The local perturbations include transitions that are split into doublets as well as transitions that have been shifted from their expected positions. The magnitude of the average coupling matrix element for the doublets was determined to be 0.0016 cm^{-1} . A comparison between the vibrational mode coupling in pyrazine and naphthalene indicates that mode coupling does not correlate with the density of states in the two molecules.

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FC10 10 min 11:16

10 μm INFRARED SPECTRUM OF TETRAHYDROFURAN: QUENCHING OF CORIOLIS INTERACTIONS IN THE VIBRATIONALLY EXCITED STATE

Anne M. Andrews, Brooks H. Pate, C. Cameron Miller, Adrian Ainetschian and Gerald T. Fraser

The 2 MHz resolution infrared spectrum of the asymmetric C-O stretching band of tetrahydrofuran (THF) at 1087 cm^{-1} has been observed using a microwave-sideband CO_2 -laser electric-resonance optothermal spectrometer. Transitions arising from ground state levels up to $V=3$ in the pseudorotation quantum number have been measured; definitive band assignments have been made for $V=0 \rightarrow V=0$, $V=0 \rightarrow V=1$, $V=1 \rightarrow V=0$ and $V=1 \rightarrow V=1$ transitions. Two additional bands are observed at higher energy which are associated with higher pseudorotation levels; although the J assignments for these bands are definitive, the excited state V assignments are not. All assignments are confirmed by microwave-infrared double resonance or precise ground-state combination differences. For all four bands, the upper-state term values are found to fit to a Watson Hamiltonian to better than 10 MHz, with a few levels not included in the fits perturbed by > 100 MHz. Precise microwave ΔV gaps give equally precise ΔV gaps for the C-O stretching vibration. In the absence of a third perturbing state, these measurements will furnish information on the vibrational dependence of the pseudorotation potential.

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FC11 10 min 11:28
MICROWAVE MEASUREMENTS OF THE $V=0 \rightarrow 1$ AND $V=2 \rightarrow 3$ PSEUDOROTATION BANDS OF TETRAHYDROFURAN

Anne M. Andrews, Brooks H. Pate and Gerald T. Fraser

The microwave spectrum of tetrahydrofuran (C_4H_8O) was first observed by Engerholm, *et al.*¹ $\Delta V=0$ transitions arising from levels up to $V = 8$ in the pseudorotation quantum number were reported. The $V = 0$ and 1 and $V = 2$ and 3 levels are strongly Coriolis perturbed and were estimated to be separated by 19.5(1.5) GHz and 45(15) GHz respectively. We have extended the microwave measurements for the $V = 0, 1, 2$ and 3 pseudorotation states in the 10 MHz to 40 GHz region using an electric-resonance optothermal spectrometer with a microwave synthesizer. The extremely weak c-type transitions between the $V = 0 \rightarrow 1$ and $V = 2 \rightarrow 3$ levels have been measured for the first time. Their assignments are verified by double resonance with 10 μm infrared transitions arising from common ground states. The $V = 0$ and 1, and $V = 2$ and 3 data sets are fit separately to a Watson Hamiltonian supplemented by a b-type Coriolis term. The standard deviations of the fits are ≈ 1 MHz and 3 MHz respectively, and the $V = 0 \rightarrow 1$ and $V = 2 \rightarrow 3$ gaps are now precisely determined as 21301(1) MHz and 46618(2) MHz. These splittings together with the precise Coriolis constants will allow a refinement of the pseudorotation potential.

¹ G. Engerholm, A. Lunz and W. Gwinn, J. Chem. Phys., **50**, 2446 (1969).

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FC12 10 min 11:40
High Resolution Infrared Study of *gauche*-1,1,2-Trifluoroethane: Intramolecular Interactions and Vibrational Mode Coupling

Sasha G. Alcott, C. Cameron Miller, Stephen C. Stone, and Laura A. Philips

The high resolution infrared spectrum of *gauche*-1,1,2-trifluoroethane (TFE) in a molecular beam in the region 3003-3007 cm^{-1} was obtained using optothermal detection. The sensitivity was increased using quadrupole focusing. When the quadrupoles had no potential difference, no spectrum was detected. The analysis of the band will be discussed, and the results will be compared with a homologous series of substituted ethanes. Previously, 2-fluoroethanol, *gauche*-1,2-difluoroethane, and *gauche*- and *trans*-1-chloro-2-fluoroethane were studied. The earlier studies show that a correlation exists between the strength of intramolecular interaction and the extent of vibrational mode coupling. 2-Fluoroethanol, with the strongest interaction, has the most coupling. *Trans*-chloro-fluoroethane, with the least interaction, shows no peak fractionation. TFE will provide a test for this model, which predicts that the extent of coupling in TFE will be between that of 2-fluoroethanol and *gauche*-1,2-difluoroethane.

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FC13 15 min 11:52

INFRARED-MICROWAVE DOUBLE RESONANCE SPECTROSCOPY OF THE C-F STRETCHING FUNDAMENTAL AND TWO PERTURBING STATES OF 2-FLUOROETHANOL

Anne M. Andrews, Brooks H. Pate, C. Cameron Miller, Laura A. Philips and Gerald T. Fraser

Last year at this meeting we presented preliminary results on the C-F stretch of the Gg' conformer (the lowest energy of the five conformers) of 2-fluoroethanol at 1038 cm^{-1} , which was observed using a microwave-sideband CO₂-laser electric-resonance optothermal spectrometer.¹ Only a fraction of the large number of transitions measured could be attributed to a single vibration. Further experiments have shown that transitions are present from two perturbing dark states in addition to the C-F stretch bright state. Microwave-infrared double resonance has been used to probe the microwave spectra of the dark states. The assignment of two complete additional bands accounts for all of the confirmed upper state energy levels and $\approx 95\%$ of the observed infrared transitions. The three bands are centered at 1039.26, 1040.93, and 1041.27 cm^{-1} . Assuming the perturbors come from the same conformer, the dark state vibrations are tentatively assigned as the $\nu_{16} + \nu_{21}$ and the $\nu_{19} + 5\nu_{21}$ combination bands. Due to the absence of a symmetry plane in this molecule, these levels can interact via anharmonic or parallel or perpendicular Coriolis coupling. For this reason, no attempt has been made to model the interaction. These measurements, combined with the results on the C-O stretch lead to a detailed characterization of the lowest frequency ν_{21} C-C torsional mode of 2-fluoroethanol. Knowledge of this vibration may permit greater understanding of the vibrational couplings in the higher frequency C-H stretching mode.

¹ C.C. Miller, A.M. Andrews, G.T. Fraser, B.H. Pate and L.A. Philips, 48th Symposium on Molecular Spectroscopy, 1993.

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FC14 10 min 12:09

AN INFRARED DOUBLE RESONANCE STUDY OF PROPYNE BY PUMPING THE WEAK $\nu_3 + 2\nu_9$ BAND, THOMAS CRONIN, JUNG-SUG GO, AND DAVID S. PERRY

In earlier work done by this group on the ν_6 , $(\nu_1 + \nu_6)$ and ν_1 bands of propyne, it was demonstrated that an IR-IR double resonance technique applied to jet-cooled polyatomics offers several experimental advantages including state selection, access to one-photon-forbidden vibrations, sub-Doppler resolution, and high sensitivity. To date, eigenstate resolved studies of IVR have focused on hydride stretches because their frequencies are high enough that the threshold energy for IVR can be reached. The goal of this work is to study IVR following excitation of some of the more general vibrations involving bends and the motion of heavy atoms.

We report here the extension of the double resonance technique to the study of the $\nu_3 + 2\nu_9$ combination band of propyne. This band carries 2% of the oscillator strength of ν_1 in propyne and is of interest in the study of IVR because it couples the $\text{-C}\equiv\text{C-}$ stretching mode and $\text{-C}\equiv\text{C-H}$ bending modes. We report the saturation spectrum of $\nu_3 + 2\nu_9$ and double resonance spectra involving $(\nu_3 + 2\nu_9)$ and ν_1 .

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FC15 15 min 12:21

A STUDY OF THE $\text{Pb}(^3\text{P}_0) + \text{O}_2(^1\Delta_g)$ REACTION WITH ULTRAVIOLET PHOTOELECTRON SPECTROSCOPY.

DARREN HAGGERSTON and JOHN M. DYKE

The HeI photoelectron spectra of atomic lead in its ground state ($^3\text{P}_0$) and first two excited states ($^3\text{P}_1$ and $^3\text{P}_2$) have been obtained in the temperature range 1080 \rightarrow 1220 K. The lead excited states were prepared *via* a near-resonant energy transfer process involving a crossed-beam reaction of atomic Pb vapour with metastable $\text{O}_2(^1\Delta_g)$, generated in a microwave discharge. An intermediate coupling scheme has been formulated to qualitatively and quantitatively account for the relativistic effects apparent in the spectrum. This model is shown to be in good agreement with both experiment and relativistic configuration interaction calculations. The conversion of ground state lead to its two lowest excited states was found to be approximately 10%.

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FC16 15 min 12:38

INFRARED LASER SPECTROSCOPY OF THE LINEAR C_{13} CARBON CLUSTER, T.F. GIESEN, A VAN ORDEN, H.J. HWANG, R.S. FELLERS, R.A. PROVENÇAL, AND R.J. SAYKALLY

The infrared absorption spectrum of the linear C_{13} pure carbon cluster was observed using a supersonic cluster beam/diode laser spectrometer. Seventy-six rovibrational transitions of an antisymmetric stretching fundamental were observed between 1808.1 cm^{-1} and 1809.7 cm^{-1} . A nonlinear least squares fit of the observed frequencies and ground and upper state combination differences lead to the following molecular parameters (cm^{-1}):
 $B'' = .0047324(6)$, $B' = .0047218(6)$, $G = 1968.96399(7)$

This represents the first definitive structural characterization of a carbon cluster in the intermediate size range between C_{10} and C_{20} . The observation of a linear carbon cluster in this size range is in apparent conflict with theoretical calculations, which predict they should exist as planar monocyclic rings.

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FC17 15 min 12:55

THE FAR INFRARED SPECTRUM OF $(\text{NH}_3)_2$ BETWEEN 80 AND 100 cm^{-1} , J.G. LOESER, J.D. CRUZAN, E. BITTEN, M. BROWN, AND R.J. SAYKALLY

Two new intermolecular vibrations of $(\text{NH}_3)_2$ have been observed by tunable far infrared laser spectroscopy in a planar jet. So far, 288 absorption lines between 80 and 90 cm^{-1} have been assigned to 32 subbands of the two vibrations. One vibration has b-type (out-of-plane) selection rules and is assigned as a torsion about the intermolecular bond axis. The other has a-type (in-plane) selection rules and is tentatively assigned as the 'geared' in-plane bend, or equivalently, the second overtone of 'donor'-'acceptor' interchange. The vibrational assignments of the new spectra and the proton tunneling dynamics in the excited states will be discussed.

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FD01 15 min 8:30

AB INITIO CALCULATION OF THE VIBRATIONAL STRUCTURE OF PHOTOELECTRON SPECTRA FOR FREE RADICALS

M. Horn and P. Botschwina

Ab initio calculations, mostly by means of the CEPA-1 method,¹ were carried out for radicals and cations of type CX_nY_{3-n} with $X, Y = F, Cl$. Most emphasis is given to the vibrational structure of the first band of the photoelectron (PE) spectra. Due to strong mode-coupling these are rather complex. Already the low-temperature PE spectrum of CCl_3 , which may be well described as a two-mode problem, shows more than 100 lines with more than 1 % relative intensity in the range $0 - 10000 \text{ cm}^{-1}$. Several of the vibrational frequencies of the cations may be compared with experimental data from matrix-isolation IR spectroscopy;² throughout the agreement is very good.

¹CEPA-1: Coupled Electron Pair Approximation, version 1; W. Meyer, J. Chem. Phys. **58**, 1017 (1973).

²M. E. Jacox, J. Phys. Chem. Ref. Data, **13** (1984), and references therein.

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FD02 15 min 8:47

VIBRATIONAL FREQUENCIES, IONIZATION ENERGIES AND HEATS OF FORMATION OF METHYL-SUBSTITUTED AMIDOGEN RADICALS

Timothy G. WRIGHT AND Terry A. MILLER

The ground states of the NH_2 , CH_3NH and CH_3NCH_3 radicals were studied *via* a variety of *ab initio* methods including SCF, MP2, CCSD AND CCSD(T). Vibrational frequencies were calculated for all ground states using all methods, where possible, and with a variety of basis sets. The final value for the ionization energy (I.E.) of the NH_2 radical was within 0.05 eV of the experimental value. It was found that the I.E.s of the substituted radicals are far from the values in a recent compilation, and a re-evaluation of the literature has been performed. Ionization energies and heats of formation of the radicals are also calculated using the *Gaussian 2* methodology.

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FD03 15 min 9:04

Potential energy surfaces for $\text{OH}(\text{X } ^2\Pi, \text{A } ^2\Sigma^+) + \text{rare gas open shell van der Waals complexes: How well can } ab \text{ initio theory predict them ?$

U. Schnupf, M.C. Heaven, D.G.Musaev, K.Morokuma

In the past few years many *ab initio* calculations have been performed to calculate potential energy surfaces for closed and open shell van der Waals complexes. The level of theory used ranges from SCF,CASSF,MRCI, to perturbation methods. To date, the most successful calculations for an open-shell system were made for OH-Ar^1 . The calculated potential energy surface for the $\text{A } ^2\Sigma^+$ state was in good agreement with the surface deducted from spectroscopic data. However, the *ab initio* calculations appeared to underestimate the depth of the $\text{X } ^2\Pi$ state potential surfaces.

In the present work we report new CEPA potential surfaces for $\text{OH}(\text{A}, \text{X})\text{-Rg}$ complexes with $\text{Rg}=\text{He}, \text{Ne}$ and Kr . For $-\text{Ne}$ and $-\text{Kr}$, comparisons between the rovibronic energies predicted from the surfaces, and those measured experimentally, will be presented. For OH-He , predications of the binding energies and geometries will be reported.

1) A.D.Esposti, H.J.Werner, J.Chem.Phys. **93**(5), 3351 (1990).

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FD04 15 min 9:21

***Ab initio* calculation of the $\text{CH}(\text{X } ^2\Pi, \text{A } ^2\Delta, \text{B } ^2\Sigma^-, \text{C } ^2\Sigma^+) + \text{Ne } (^1\text{S})$ potential energy surfaces, U. Schnupf, M.C. Heaven, D.G.Musaev, K. Morokuma**

We report multireference configuration-interaction calculations for the four lowest adiabatic doublet potential energy surfaces of the $\text{CH}(\text{X } ^2\Pi, \text{A } ^2\Delta, \text{B } ^2\Sigma^-, \text{C } ^2\Sigma^+) - \text{Ne } (^1\text{S})$ open shell van der Waals molecule. The CH-Ne van der Waals complex is found to be bound by about 30.5 cm^{-1} in the electronic ground state with a T-shaped geometry. The A,B and C state potential energy surfaces have two minima at collinear geometries which correspond to isometric CH-Ne and Ne-CH structures. The dissociation energies for the excited states range from 35 cm^{-1} to 45 cm^{-1} , where the global minima in each excited state can be found at the linear CH-Ne configuration. The calculated potential energy surfaces have been fitted to an analytical function and used to calculate bound rovibrational levels of the CH-Ne complex.

In order to investigate why the $\text{CH}(\text{C } ^2\Sigma^+)\text{-Ne}$ complex was not seen experimentally, we have calculated transition moments for the transition ground state to all three excited states.

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FD05 15 min 9:38

Comparative *ab initio* study of bending potentials for MgNC and CaNC

Keisaku Ishii, Tsuneo Hirano, and Koichi Yamashita

The ground state potential energy surfaces of MgNC and CaNC were calculated by highly correlated *ab initio* single-reference Averaged Coupled Pair Functional method. The basis sets used are [5s3p2d1f+1s1p] for C and N, [6s5p3d1f] for Mg and [10s10p6d2f] for Ca, respectively. Mg L-shell core-valence correlation and Ca M-shell core-core correlation were included for MgNC and CaNC, respectively. Both species are considered as ionic compound formed of M^+ and CN^- in their ground $2\Sigma^+$ electronic states. Therefore the directionalities of metal-NC bonding in MgNC and CaNC are very small and potential energy surfaces for bending motion are extremely shallow. Theoretically calculated harmonic frequencies of bending mode are 90 cm^{-1} for MgNC and 60 cm^{-1} for CaNC, and the barriers of isomerization to meta-stable MgCN and CaCN are 2160 cm^{-1} and 1950 cm^{-1} , respectively. Although two molecules are isovalent, the shapes of their bending potential are quite different. The bending potential for MgNC is essentially of harmonic nature, while that for CaNC has quite anharmonic and anisotropic character (Fig. 1). For CaNC, the first excited state of v_2 mode in harmonic approximation reaches the strong anharmonic region of bending potential. Furthermore, the second excited state in harmonic approximation reaches the region where bending angle strongly couples with the CaN bond length (Fig. 2). In the region where bending angle is smaller than 120 degree, the CaN bond length becomes longer than the value at linear equilibrium geometry.

Such difference in bending potential between MgNC and CaNC is one of the reason why centrifugal distortion constants up to tenth order are needed to interpret the microwave spectrum of CaNC¹ while only within sixth order terms are necessary for MgNC.²

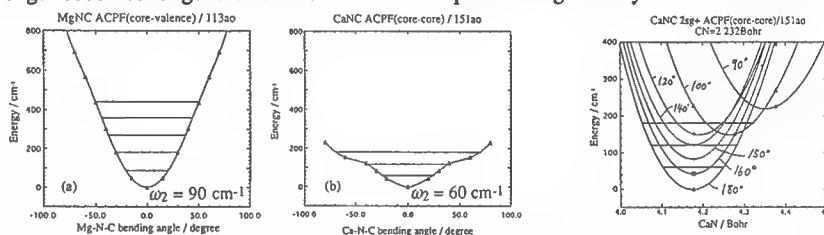


Fig. 1 (a) Bending potential of MgNC ($X\ 2\Sigma^+$), (b) Bending potential of CaNC ($X\ 2\Sigma^+$)

1. Steimle *et al.* *Astrophys. J.* **410**, L49 ('93). 2. Kawaguchi *et al. ibid.* **406**, L39 ('93); Ishii *et al. ibid.* **410**, L43 ('93)

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FD06 10 min 9:55

A THEORETICAL INVESTIGATION OF THE CH_2CN AND CH_2NC RADICALS

R. Oswald and P. Botschwina

The CH_2CN and CH_2NC radicals have been studied by the MR-ACPF¹ and CEPA-1² methods, using a basis set of 108 contracted Gaussian-type orbitals. Almost identical equilibrium geometries were obtained with both methods. The MR-ACPF results are: a) CH_2CN : $r_e(\text{CH}) = 1.079\text{ \AA}$, $\alpha_e(\text{HCH}) = 120.0^\circ$, $R_{1e}(\text{CC}) = 1.395\text{ \AA}$, and $R_{2e}(\text{CN}) = 1.175$; b) CH_2NC : $r_e = 1.077\text{ \AA}$, $\alpha_e = 122.9^\circ$, $R_{1e}(\text{CN}) = 1.332\text{ \AA}$, and $R_{2e}(\text{NC}) = 1.204\text{ \AA}$. The wavenumbers of the CH_2 wagging mode of CH_2CN is calculated to be 629 cm^{-1} , (absolute IR intensity: 51 km mol^{-1}) in good agreement with the recent high-resolution study of Tanaka and coworkers.³ The CH_2 rocking vibration ($\omega_8 = 1040\text{ cm}^{-1}$) is calculated to be about half as strong. The present calculations support the assignment of a peak observed at 1027 cm^{-1} in the argon matrix spectrum⁴ to this vibration.

¹MR-ACPF: Multiconfiguration Reference Average Coupled Pair Functional; R. J. Gdanitz and R. Ahlrichs, *Chem. Phys. Lett.* **143**, 413 (1988).

²CEPA-1: Coupled Electron Pair Approximation; W. Meyer, *J. Chem. Phys.* **58**, 1017 (1973)

³K. Tanaka, T. Harada, Y. Sumiyoshi, and T. Tanaka, contribution B-22 at the 22nd International Symposium at Free Radicals, Doorwerth, 1993.

⁴M. E. Jacox, *Chem Phys.* **43**, 157 (1979); private communication (1994).

FD07 15 min 10:07

THE EQUILIBRIUM STRUCTURE AND WAVENUMBERS OF TOTALLY SYMMETRIC VIBRATIONS FOR H₂CCCC CALCULATED AB INITIOP. Botschwina and M. Oswald

Free cumulene carbenes H₂C_n (n ≥ 3), are of substantial current interest, mainly due to their importance in interstellar cloud chemistry¹. Following our previous work on H₂CCC² we have carried out large-scale CCSD(T) calculations,³ using a basis set of 220 contracted Gaussian-type orbitals and correlating all electrons. The equilibrium geometry is: r_e (CH) = 1.0810 Å, α_e (HCH) = 119.5°, R_{1e} (C₍₁₎C₍₂₎) = 1.3062 Å, R_{2e} (C₍₂₎C₍₃₎) = 1.2902 Å, and R_{3e} (C₍₃₎C₍₄₎) = 1.2866 Å. The harmonic vibrational wavenumbers for totally symmetric modes are (in cm⁻¹): $\omega_1 = 3164$, $\omega_2 = 2117$, $\omega_3 = 1709$, $\omega_4 = 1393$, and $\omega_5 = 905$.

¹P. Thaddeus, C. A. Gottlieb, R. Mollaghababa, and J. M. Vrtilik, J. Chem. Soc. Faraday Trans. **89**, 2125 (1993)

²C. A. Gottlieb, T. C. Killian, P. Thaddeus, P. Botschwina, J. Flügge, and M. Oswald, J. Chem. Phys. **98**, 4478 (1993)

³Coupled Cluster method with single and double excitation operators and a quasiperturbative treatment of the effects of connected triple excitations; K. Raghavachari, G. W. Trucks, J. A. Pople and M. Head-Gordon, Chem. Phys. Lett. **157**, 479 (1989).

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FD'01 15 min 10:30

Radiofrequency/optical double resonance spectroscopy of He₂.

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Using a Ti-sapphire laser and a radiofrequency wave guide in combination with a fast, mass-selected beam of He₂ in the meta-stable a ³Σ_u⁺ state, we have measured the fine structure splittings in the a (v=0, N=25,27,29 and v=2, N=7,9,11) levels to a precision better than 15 kHz. The experimental spin-spin and spin-rotation coupling parameters λ and γ (in MHz) are well represented as second order polynomials in the internuclear separation, R (in atomic units):

$$\lambda(R) = -1101.221 + 1349.2241(R-2) - 427.22254(R-2)^2$$

and

$$\gamma(R) = -2.39823 + 4.70583(R-2) - 3.27895(R-2)^2$$

Using these polynomials and the nuclear wavefunctions calculated from the a-state potential of Yarkony[1], we can reproduce the experimental values of λ and γ within 0.01 MHz

The laser excites molecules from the a-state to quasibound levels in the c ³Σ_g⁺ state, which decay by tunneling through the potential barrier of the c-state. The experimental linewidths agree well with those calculated using the empirical c-state potential of Lorents et al. [2]

[1] D.R. Yarkony, J. Chem. Phys. **90**, 7164 (1989).

[2] D.C. Lorents, S.R. Keiding, and N. Bjerre,
J. Chem. Phys. **90**, 3096 (1989).

FD'02 15 min 10:47

DEVELOPMENT OF A PULSED MOLECULAR BEAM FOURIER TRANSFORM MICROWAVE SPECTROMETER IN THE 26 TO 40 GHz REGION

I. Merke, H. Dreizler, and W. Stahl

After pulsed molecular beam (MB) Fourier transform microwave (FTMW) spectroscopy has become a widely used technique for the investigation of stable molecules, van der Waals clusters, free radicals, and recently also ions, we felt it worth while to extend the frequency range covered by this method to a higher limit. In order to minimize the use of expensive microwave equipment in the 26-40 GHz range, the polarizing pulses are produced by a microwave synthesizer in the range from 13 to 20 GHz with subsequent frequency doubling. For down conversion of the free induction decay a subharmonic mixer is used. As in our MB-MWFT spectrometers below 26 GHz the molecular beam is pulsed through one of the mirrors of the Fabry-Perot cavity. In this way also at high frequencies very narrow lines and a high resolution is achieved.

Technical details of the apparatus and some spectroscopic applications will be presented.

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FD'03 15 min 11:04

A MILLIMETER-WAVE STUDY OF THE HCCCS AND DCCCS RADICALS

M. C. McCarthy, J. M. Vrtilek, E. W. Gottlieb, F.-M. Tao, C. A. Gottlieb, and P. Thaddeus

Over 100 rotational transitions of the free radicals HCCCS and DCCCS, in both spin components of their 2Π electronic ground state and in several low-lying vibrationally excited states, have been observed by millimeter-wave spectroscopy in the 80-400 GHz region. Prior to this work, HCCCS had only been observed in the $2\Pi_{1/2}$ ground state spin component.¹ The spin-orbit constant, determined here for the first time, supports the conclusion that, unlike HCCS,² the unpaired electron is localized primarily on carbon, contrary to *ab initio* calculations which predict significant electron density on the sulfur atom. *Ab initio* calculations also predict a bent ground state with $2A'$ symmetry at several levels of theory. At the highest level of theory (QCISD) the 2Π state is only slightly higher ($\sim 450\text{ cm}^{-1}$) in energy. Recent progress made in identifying both isomeric structures and in determining the ordering of the low-lying vibrational states of this interesting radical will be discussed.

¹ Y. Hirahara, Y. Ohshima, Y. Endo, Talk MG10, 48th International Symposium on Molecular Spectroscopy, Columbus, Ohio, 1993.

² J. M. Vrtilek, C. A. Gottlieb, E. W. Gottlieb, W. Wang, and P. Thaddeus, *Ap. J. (Letters)* **398**, L73, (1992).

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POINT DEFECT ACTIVITY IN AMORPHOUS SOLID WATER AND THE POSSIBLE ROLE OF DEFECT ACTIVITY IN THE GLASS TRANSITION, M. FISHER AND J.P. DEVLIN

It has been proposed that low temperature phase transformations in hydrogen-bonded solids such as ice depend on the concentration and mobility of orientational (Bjerrum L) point defects. If defect activity is necessary for the growth of crystalline ice from other phases of water (such as liquid water or amorphous solid water), it is important to understand the behavior of orientational defects in these systems. In this study, the isotopic scrambling of D_2O molecules isolated in amorphous H_2O ice by mobile point defects has been used as a probe of defect mobility at temperatures below the glass transition temperature. The sequential passage of defects through sites in the ice lattice initially occupied by D_2O molecules results in the formation of spectroscopically distinguishable deuterated species in the ice lattice. From the infrared spectra of these samples, the change in concentration of these spectroscopically distinguishable species is then followed with time and over a range of temperatures, enabling the determination of kinetic parameters relating to defect mobility. A mechanism for the isotopic scrambling process in amorphous ice below the glass transition temperature has been proposed. This mechanism invokes point defect motion to explain the experimentally observed changes in concentration of deuterated species with respect to time. The isotopic exchange data seems to indicate a lack of significant molecular diffusional motion (fluidity) in amorphous ice at temperatures just below the glass transition temperature. This finding is inconsistent with the recent conjecture that molecular diffusional motion plays a significant role in the glass transition which occurs in amorphous ice at approximately 130 K.^{1,2}

¹ G.P. Johari, A. Hallbrucker, and E. Mayer, *J. Chem. Phys.*, **95**, 6849 (1991).

² A. Hallbrucker, E. Mayer, and G.P. Johari, *J. Phys. Chem.*, **93**, 7751 (1989).

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FD'05 15 min 11:38

ANHARMONICITY OF THE VIBRATIONS OF SiC₂ AND Si₂C AT 2000 K, R. W. SCHMUDE, JR. AND K. A. GINGERICH

Butenhoff and Rohlfing¹ report that SiC₂ has an anharmonic ground state, based on Laser-induced fluorescence studies. Presilla-Marquez and Graham² report that Si₂C is a "floppy" molecule with a bending frequency of 166 cm⁻¹. Therefore SiC₂ and perhaps Si₂C may have some anharmonic behavior which can show up in Knudsen effusion mass spectrometric studies as is the case for C₃.

A thorough Knudsen-effusion mass spectrometric study of SiC₂ and Si₂C was carried out; a total of 46 data sets of SiC₂ and 52 data sets of Si₂C over a temperature range of 1760-2080 K were obtained. Although the main objective of this study was to measure the atomization enthalpies of small silicon-carbide clusters; we also wanted to determine the effect of any anharmonicity of SiC₂ and Si₂C on the experimental results. It is concluded that the anharmonic behavior of SiC₂ and Si₂C had little effect on the experimental results at ~2000 K. Atomization enthalpies of $\Delta H_{a,0}=1247\pm 7$ and $\Delta H_{a,0}=1048\pm 10$ kJ mol⁻¹ are selected for SiC₂ and Si₂C.

1. T. J. Butenhoff and E. A. Rohlfing, J. Chem. Phys. 95, 1 (1991).
2. J. D. Presilla-Marquez and W. R. M. Graham, J. Chem. Phys. 95, 5612 (1991).

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FD'06 10 min 11:55

SELECTIVE LASER SPECTROSCOPY OF MOLECULAR IONS UO₂²⁺ ADSORBED ON DISPERSE SiO₂ SURFACE

YU. D. GLINKA, and T. B. KRAK

Low-temperature luminescence spectra of molecular ions UO₂²⁺ adsorbed on disperse SiO₂ surface were investigated under selective laser excitation. It was determined that molecular ions are very sensitive luminescent probes for investigations of active in adsorption centers (AC) on disperse silicon dioxide surface. Different AC causes many elementary luminescence spectra. It was established uranyl ions link with the surface by means of water molecules. H₂O-molecules coordinate uranium in water-uranyl complexes and take part in the formation of adsorption bonds. One can observe two AC types corresponding to physical and chemical adsorption states [1]. To our mind, the first type complexes are fixed on surface hydroxyls by hydrogen bonds. The chemisorbed complexes are formed under interaction of water molecules in water-uranyl complexes with surface silicon, bridging oxygen atoms, and surface structural defects.

It is established that UO₂²⁺ ions are fixed on the surface by means of two or three water molecules forming water-uranyl complexes. Active in adsorption centers for these complexes are surface silanol groups.

1. Glinka Yu.D., Degoda V.Ya., Krak T.B. et al. // J. Appl. Spectr. 1993. 59, No 3-4. P.286-292.

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FD'07 15 min 12:07

The absorption spectra of the Cu(II) beta-diketonates vapours in the 115 - 300 nm region

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The high temperature vapour absorption spectra of Cu(gfac)₂, Cu(dpm)₂ (gfac, dpm - 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate, 2,2,6,6-tetramethyl-3,5-heptanedionate anions, respectively) have been measured on Seya-Namioka type spectrophotometer with a resolution of 5 Å in the 115 - 300 nm region. The hydrogen lamp was used as a radiation source. The heated and vacuum-tight quartz cells with MgF₂ windows were used.

The concentration of Cu(II) beta-diketonates was calculated from saturated vapour pressure data. The absorption cross sections of Cu(II) beta-diketonates vapours were calculated. It was shown the obtained values correspond to the known extinction coefficients in the 220-300 nm region of these compounds dissolved in nonpolar solvents.

The intense absorption bands in the wavelength region of 140-170 nm were determined. Using the known molecular orbital calculations for Cu(dpm)₂ the absorption bands observed about 150, 210, 250 nm can be interpreted as the metal to ligand charge-transfer e-transitions and the absorption bands observed about 170, 300 nm - as the ligand e-transition bands.

The obtained spectral data of these compounds were used for an aiming choose of the wavelength for the photochemical vapour deposition of metal films.

FD'08 15 min 12:24

SPECTROSCOPIC EVIDENCE FOR HYDROGEN MIGRATION IN HALO-CYCLOHEXADIENYL RADICALS IN SOLID ARGON, P. HASSANZADEH and J. H. MILLER

Halogen atoms, produced by passing a mixture of halogen and argon through a microwave discharge, are cocondensed with a mixture of benzene in argon on a 12K sapphire window. When the halogen is either fluorine or chlorine the absorption features observed are the same as those obtained from the reaction of hydrogen atoms with fluorobenzene and chlorobenzene, and are assigned to fluoro and chlorocyclohexadienyl radical isomers, respectively. In the absence of rearrangement, addition of a halogen atom to benzene is expected to produce initially only an ipso halocyclohexadienyl radical. Absence of phenyl and halobenzene absorptions on initial sample deposition and observation of other cyclohexadienyl isomers suggest that the ipso isomers undergo internal rearrangement via hydrogen migration around the benzene ring. In our experiments, the halogen atoms mix and react with the precursors in the gas phase above the matrix surface; however, rearrangements can occur in both the gas phase or in the matrix upon photolysis.

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FD'09

15 min

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THE NATURAL ABSORPTION OF AQUAPHILOUS CRYSTAL SEMICONDUCTORS, N.P.NETESOVA

Earlier it was shown for the fundamental absorption edge of polar crystals to be in close agreement with the absorption discontinuity of limiting dilute solutions of these crystals. In this connection the united one oscillator model was proposed for the description electronic characteristics both crystals and their solutions.

In development of these ideas the bioscillator model is calculated for the natural absorption of the crystal semiconductors. The first electron oscillator equation and the second electron oscillator equation are examined for the direct transitions of the valence electrons and the indirect transitions of the conduction electrons correspondingly taking account of the oscillator system connectedness determined experimentally from absorption spectra of the dilute solution crystals.

The procedure and the equations are presented for the computations of the absorption integrals of the condensed medium and gases, the plasma, natural, effective, restricted band and dissipated energy for direct and indirect electron transitions in crystals accordingly from the natural absorption spectra of their solutions at the infinite dilution corrected for the state change energy. It is submitted the function of electronic losses and effective number for crystals computed by reflectance spectrum.

The theoretical formulations are in agreement with the investigated dispersion on optical constants of polar crystal solutions near the absorption edge. In going from crystal to the solution with reducing electronic density short-wave maximum of the fundamental absorption generated by direct transitions and long-wave maximum, generated by electron phonon interaction displace in the region of a lesser wavelength, decrease and disappear in the ratio of electronic densities correspondingly amounted to 1000.

The proposed approach is directed to the use molecular spectrum data for the formation and characterization of low-dimensional structures.

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 KOZIN, I.N.--RG11
 KRAEMER, W.P.--RG08
 KRAK, T.B.--FD'06
 KRESZOWSKI, D.H.--TB11
 KRONFELDT, H.D.--ME13,
 ME03, ME09
 KRUPNOV, A.F.--WF13
 KRUTULES, K.A.--RB08
 KUCZKOWSKI, R.L.--TC07,
 TC01, TC02, WF05
 KÜHNEMANN, F.--TE'05, FB16
 KUKUEVA, V.V.--FA15
 KUWATA, K.T.--RD06

L

LAANE, J.--TF09, TF13
 LAFFERTY, W.J.--TD10, FB10,
 ME01
 LAFYATIS, G.--FA04
 LAI, V.--RH09
 LANGE, N.--RA'04
 LANGENBERG, J.D.--WH12,
 WH10
 LAUSH, C.T.--FC05
 LAVENDER, H.B.--FC07
 LAWRENCE, W.G.--TG13,
 TG11, TG12
 LAZAREV, V.V.--ME06

LE, L.D.--RB05
 LEACH, G.W.--TA02
 LEE, T.J.--RG11
 LEE, Y.P.--RF10
 LEES, R.M.--TD09, TD01, FB11,
 TD02, TD06
 LEHMANN, K.K.--RA'07, FB03,
 FB08, TE02
 LEMBACH, G.--TF03
 LEONARD, JR., J.D.--TB10
 LEOPOLD, K.R.--FC03, WF04,
 WF06
 LEROI, G.E.--TG08
 LeROY, R.J.--WE04, RE03
 LI, B.H.--MH11, MG14
 LI, L.--FA09, WG09, FA10
 LI, S.--TG01, TG02
 LI, X.--MG05
 LI, Y.--RG11
 LI, Z.--TF04
 LI, Z.--RE04
 LIEDTKE, M.--WF13
 LIEVIN, J.--FB07
 LIM, E.C.--TF01, RC09
 LIM, M.--TB06, TB07
 LIN, H.S.--TG13
 LIN, S.H.--TB08
 LIND, J.--TF14
 LINEBERGER, W.C.--TA02
 LINTON, C.--MH02
 LISY, J.M.--RD07, RD08, FC05
 LO, W.R.--RF10
 LOESER, J.G.--FC17
 LONGHI, G.--WE02
 LOVAS, F.J.--TC12, WF06, TC09,
 TC10, WF09, TC13
 LOW, R.J.--FC01, RD02
 LU, K.T.--TF07, TF08
 LU, S.P.--TB03
 LU, Z.F.--TD03
 LUCCHESI, R.L.--FB14, FB15
 LYYRA, A.M.--FA09, WG09,
 FA10

M

MA, E.--RH09
 MAHONEY, K.I.--FA11, WH05,
 TA14
 MAIER, J.P.--WA03
 MALATHY DEVI, V.--ME07,
 ME08, ME12
 MALLOY, R.--RF'03, TC10
 MANEA, V.--TF10
 MANK, A.--WG05, TH06
 MANTZ, A.W.--RH02
 MARIAN, C.--RC01
 MARICQ, M.M.--RD03
 MARSHALL, M.D.--FC02
 MARTIN, C.H.--RC04
 MARTIN, J.D.D.--WG05
 MASON, M.A.--RA'07
 MATHEWS, C.W.--FA11, WH06,

WH05, TA14
 MATTAR, S.M.--RF03, RC07,
 MH14
 McCARTHY, M.C.--FD'04
 McCARTHY, P.K.--TB12
 McCORD, J.E.--MH03, MH04,
 WH14
 McDOWELL, R.S.--TE01
 McIntOSH, A.L.--FB13, FB14
 McKELLAR, A.R.W.--RE03,
 RD01
 McRAE, G.A.--RH14
 MEADS, R.--FB15
 MELLAU, G.--FB04
 MENARD, I.--ME14
 MENARD-BOURCIN, F.--ME14
 MERER, A.J.--RB02, RH09,
 MH08, MH09
 MERKE, I.--FD'02
 MERKT, F.--TH11
 METHA, G.F.--MH09
 MEUSEL, I.--ME13, ME09
 MICHALAK, R.--WG07
 MIKAMI, N.--TH09
 MILLER, C.C.--FC10, FC13,
 FC12, FC08
 MILLER, C.E.--RH07
 MILLER, J.H.--FD'08
 MILLER, R.E.--RE07, RE11,
 RE08, RE12
 MILLER, T.A.--FD02, RD12, RD11,
 RH16, MG06, WH03, WE07,
 TF05, RD10
 MINAEV, B.F.--FA15
 MISRA, P.--MF10, MG04, TA09
 MLSNA, T.E.--MG06
 MOAZZEN-AHMADI, N.--RD01
 MOHARERRZADEH, M.--RC02
 MOLLAAGHABABA, R.--RE13,
 RE14
 MOMOSE, T.--MF02, MF04
 MORBI, Z.--RH10, RH11, RH12
 MORETTI, A.--TD01
 MORITA, N.--TH08
 MOROKUMA, K.--FD03, FD04
 MORRIS, JR., D.L.--TB09
 MORSE, M.D.--TA04, WH12,
 WH11, WH10, WA04
 MORUZZI, G.--TD04, TD01,
 TD06
 MOULE, D.C.--RG12, WH09,
 WH08
 MUENTER, J.S.--RE04
 MUKHOPADHYAY, I.--TD09
 MÜLLER, H.S.P.--TF02, RF'05,
 RF'04
 MÜLLER-DETHLEFS, K.--TF03
 MULLIN, A.S.--RH01
 MURAD, E.--RD04
 MURCRAY, D.G.--RH04
 MURCRAY, F.J.--RH04
 MURRAY, J.E.--FA03
 MUSAEV, D.G.--FD03, FD04

N

NAGASHIMA, U.--TH04
 NALIVAICO, S.E.--WH07
 NASH, C.S.--RG03
 NAZ'MOV, V.P.--FD'07
 NEFF, W.A.--WF01
 NELSON, D.D.--RE14
 NEMUKHIN, A.V.--TG14, RG05
 NETESOVA, N.P.--FD'09
 NGUYEN, T.--WG05
 NIKITIN, A.--FB09
 NODA, C.--ME02
 NOEL, M.--FB11
 NOERREGAARD, A.--FD'01
 NOVICK, S.E.--FC02
 NUR, A.H.--MG04, TA09
 NUTAITIS, C.--TF14

O

O'BRIEN, J.P.--FB05
 OESTERLING, L.C.--RH05,
 WF12, RF'02
 OGATA, T.--MG02, MG03
 OGILVIE, J.F.--WE09, WE08
 OGURTSOV, A.N.--MF14
 OHASHI, N.--FC06
 OHDE, K.--RA'03
 OHSHIMA, Y.--MG10, MG02,
 MG03
 OKA, T.--TE'05, TE'06, RA02,
 MF02, MF03, MF04, MF05,
 FB16
 OKUMURA, M.--RD05, RD06
 OKUNISHI, M.--TD05
 OLSON, W.B.--ME01
 ORTIGOSO, J.--WE11, WE12
 OSWALD, M.--RG06, FD06, FD07
 OVERLY, J.A.--RB03
 OWRUTSKY, J.C.--TB05, TB04
 OZIER, I.--TE'01, TE'02

P

PANOV, S.I.--WH03, WE07
 PARKINSON, W.H.--FA03
 PARMENTER, C.S.--TB03
 PATE, B.H.--WE12, FC10, FC13,
 FC11
 PAULSE, C.D.--RH05
 PAVLENKO, V.S.--WH07
 PEARSON, J.C.--WF10, WF11,
 RF'02, FB03
 PEERS, J.R.D.--MH02
 PENDERGAST, P.--RE09, RC05
 PERRIN, A.--RH06, RH03, RH04
 PERRY, D.S.--FC14
 PERRY, F.--RF06
 PERSON, W.B.--TG09
 PESTRYAKOV, A.N.--MF12
 PETERSON, D.B.--ME11
 PETKIE, D.T.--RF'01

PFANSTIEL, J.F.--TF06
 PHILIPS, L.A.--FC13, FC12,
 FC09, FC08
 PHILLIPS, C.M.--TF14
 PHILLIPS, J.A.--WF04
 PIBEL, C.D.--RA'03
 PIERRE, G.--FB09
 PILGRIM, J.S.--WH02, WH01
 PINE, A.S.--ME10, FB09, RE10
 PINEGAR, J.C.--WH10
 PISARCHIK, A.--FB01
 PITZER, R.M.--RC10
 PLÍVA, J.--RB04, RB05, FB04
 POLAVARAPU, P.L.--TE04,
 TE05, TE06
 POLAVIEJA, G.--RG10
 POLIK, W.--FB05
 POLYANSKY, O.L.--WE14
 PONOMAREV, Yu. N.--ME06
 PRATT, D.W.--TF06
 PREDOI, A.--FB11
 PROCHASKA, F.T.--RF06
 PROVENÇAL, R.A.--FC16
 PUSTOGOV, V.V.--ME13, ME03

Q

R

RAFFERTY, B.D.--RA03
 RAIBLE, D.--TF14
 RAJARAM, B.--RA'06
 RAKOWSKY, S.--TA01
 RAM, R.S.--RH14, MH05, MH07,
 MH06
 RAMADAS, K.--WF01
 RAO, K.N.--MF01, FB04
 RAY, M.--FA04
 REICHE, M.--RB12
 REZNIKOVA, E.F.--FD'07
 RHEE, W.--RE08
 RICHARD, E.C.--TF07, TF08
 RINSLAND, C.P.--RH04, ME07,
 ME08, ME12
 RITTBY, C.M.L.--TG06
 ROBB, II, J.B.--RB09
 ROBBINS, D.L.--WH02
 ROBIETTE, A.G.--FB09
 ROHLFING, E.A.--RA'01, RA'02
 ROSS, K.A.--RH02, WF01, RH01
 ROSS, S.--RA01
 ROWLAND, B.--MF07
 RUCKSTUHL, A.F.--FA05
 RUSSON, L.M.--WH11
 RZHEVSKY, O.S.--WH07

S

SADYGOV, R.G.--RC09
 SAIGUSA, M.--TF01
 SAKAGUCHI, K.--MG09
 SALECK, A.H.--WF13
 SALZBERG, A.P.--RD10

SAMMYNAIKEN, R.--RF03
 SAMUNI, U.--TF11
 SASTRY, K.V.L.N.--WF10,
 WF11, RF'02
 SATO, K.--TH04
 SAVCHENKO, E.V.--MF14
 SAYKALLY, R.J.--FC17, FC16
 SCAPPINI, F.--MG13
 SCHICK, E.--RG06
 SCHIEDER, R.--WF13
 SCHMITT, M.--TF02
 SCHMUDE, JR., R.W.--FD'05
 SCHNUPF, U.--FD03, FD04,
 RD09, RD13
 SCHOWEN, S.--RH01
 SCHWENDEMAN, R.H.--TD08
 SCHWENTER, N.--TG11
 SCOLES, G.--FB03, FB08, TE02,
 FA06
 SCURLOCK, C.T.--MG12
 SEARS, T.J.--TA07, TA08
 SEEGER, S.--RC11
 SELEGUE, T.J.--RD07
 SENENT, M.L.--RG12
 SERGEEV, G.B.--TG14
 SETZER, K.D.--WH13
 SHARMA, R.C.--MH13
 SHARPE, S.W.--TE01
 SHAVITT, I.--RC03, RC06
 SHEN, M.--FC09
 SHESTAKOV, O.--MH15, WH13
 SHIBA, Y.--TH04
 SINGER, S.J.--FC07
 SLANGER, T.G.--FA02
 SMEYERS, Y.G.--RG12
 SMITH, M.A.H.--ME07, ME08,
 ME12
 SMITH, P.G.--TB01
 SNAVELY, D.--RB03
 SOBHANADRI, J.--TC12
 SOLINA, S.A.B.--FB05
 SOLODOV, A.M.--ME01
 SORIANO, G.M.--TD08
 SOVA, R.M.--ME05
 SPAIN, E.M.--WH10
 SPEARS, K.G.--MF10
 SPIELFIEDEL, A.--RC08
 SPYCHER, R.M.--TC06
 STAHL, W.--FD'02
 STEIMLE, T.C.--MG12, MH10,
 MH11, MG14
 STEINFELD, J.--TD12
 STEINHOFF, R.A.--MF01
 STEPHENS, J.A.--TH12
 STEVENS, J.E.--TC13, RG04
 STEEVES, M.C.--MH14
 STICKLAND, R.J.--TH13
 STIENKEMEIER, F.--FA06
 STÖCK, C.--MG05
 STOECKEL, F.--TE03
 STONE, S.C.--FC12
 STONE, T.A.--TB03
 STORK, W.D.--FC05

STRATTON, J.R.--TB02, TB01
 STROH, F.--TD11
 STROINOVA, V.N.--ME06
 STROW, L.L.--ME05
 STRUMIA, F.--TD01
 STWALLEY, W.C.--WG09, FA10,
 WG08, WG10
 SU, Y.--TF04, RD03
 SUDHAKARAN, G.R.--TD09
 SUENRAM, R.D.--TD10, TC13,
 MG11, FC04, WF06, TC09,
 TC10, WF09
 SUMIYOSHI, Y.--MG08
 SUMPF, B.--ME13, ME03, ME09
 SUZUKI, S.--TB08
 SWARTZ, J.C.--TD07
 SZCZEPANIAK, K.--TG09
 SZCZEPANSKI, J.--RF04, TG07
 SZE, N.S.-K.--MH12
 SZENTE, J.J.--RD03

T

TAGUE, JR., T.J.--TG05, RB12
 TALEB-BENDIAB, A.--MG13,
 TE'07, TE'03
 TAN, X.Q.--MG06, WF05
 TANAKA, K.--MG10, MG08,
 MG09, FB17
 TANAKA, T.--TE'04, MG08,
 MG09, FB17
 TAO, F.M.--RE05, RG02, RE06,
 FD'04
 TCHANG-BRILLET, L.--TH03
 TEMPS, F.--MG05
 TEMSAMANI, M.A.--FB02,
 FB01
 TENNYSON, J.--RG10, WE14
 THADDEUS, P.--MA01, FD'04
 THAKUR, S.N.--MH13
 THOMAS, M.E.--WF06, ME05
 THOMPSON, C.A.--TG04
 THOMPSON, W.E.--RF02
 THONG, J.J.--RD01
 THORNE, A.P.--FA03
 TIKHOMIROV, B.A.--ME06
 TIMMERMANS, J.H.--TE02
 TOBIASON, J.D.--RA'01, RA'02
 TOBIN, D.--ME05
 TOPP, M.R.--TB02, TB01
 TRETYAKOV, M.Yu.--WF13
 TROE, J.--TE03, RA'04
 TROXLER, T.--TB02, TB01
 TSAI, B.P.--TA10
 TSAI, C.C.--FA10, WG08
 TSANG, S.--RE13
 TSCHOPP, S.L.--TC03
 TUBERGEN, M.J.--TC01, TC02

U

ULENIKOV, O.N.--WE06
 UNGER, I.--RF03

URBANSKI, K.--FA09, WG09
 UTTAM, K.N.--MH01
 UY, D.--TE'06, RA02

V

VALA, M.--RF04, TG07
 VALENTIN, A.--RH06, RB04
 VAN ORDEN, A.--FC16
 VANDER AUWERA, J.--FB12,
 FB06
 VANDERMEULEN, D.L.--MF10
 VAN ZEE, R.J.--TG01, TG02
 VARBERG, T.D.--FC01, RD02,
 TD11
 VASCONCELLOS, E.C.C.--TD02
 VELAZQUEZ, J.--FA01
 VRTILEK, J.M.--FD'04

W

WAGENER, V.--WF07
 WALKER, A.R.H.--FC02
 WALKER, K.A.--RE02
 WALKER, R.A.--TF07, TF08
 WALTERS, V.A.--TF14
 WANG, H.--FA10, WG10
 WANG, J.--RA'06
 WANG, S.--TG06
 WANG, Y.--WF08
 WANG, Z.--FB14
 WARD, C.--WF08
 WARNER, H.E.--RF'03, WF08,
 TC09, WF09
 WASCHULL, J.--ME13, ME09
 WATEGAONKAR, S.--TF12
 WATSON, J.K.G.--WE10, RG09,
 MG13
 WATSON, P.--TD10
 WATTSON, R.B.--ME04
 WEBER, A.--RH08, ME01
 WEHLBURG, C.--RF04
 WEIBEL, S.--TE04
 WEIBRECHT, J.--MG05
 WEISSHAAR, J.C.--TF07, TF08
 WELIKY, D.P.--MF02, MF03
 WELTNER, JR., W.--TG01, TG02
 WESTRICK, N.--TF10
 WHANG, T.J.--FA10
 WHITE, J.B.--RH12
 WHITMAN, C.J.--FC01
 WILLEY, D.R.--WF01, RH01
 WILLIAMSON, J.M.--RD12,
 RD11, MG06, TF05
 WILLEY, D.R.--RH02
 WILLNER, H.--WE01
 WINNEWISSER, B.P.--RH04,
 MF01, FB04
 WINNEWISSER, G.--WF13
 WINNEWISSER, M.--WF07,
 MF01, FB04
 WRIGHT, T.G.--FD02, TF03
 WU, M.--TA07, RE11

X

XU, L.H.--TD04, FB11, TD02,
TD06, TD03
XU, L.W.--WF05
XU, S.--TE01
XU, Y.--TE'03
XUE, G.--RB14

Y

YANG, M.C.--MG06, RD10
YANG, X.--FB03, ME02
YAMADA, C.--TD05
YAMADA, K.M.T.--WF13
YAMANOUCHI, K.--RA'03
YAMASHITA, K.--FD05
YEH, C.S.--WH01
YIANNOPOULOU, A.--FA09,
WG09
YOKOYAMA, K.--TA02
YOSHINO, K.--FA03
YURTAEVA, E.M.--MF13
YURTSEVEN, H.--RB13

Z

ZACHMANN, G.--RB12
ZARE, R.N.--TH11
ZEWAIL, A.H.--RA04
ZHANG, K.Q.--RH10, RH12,
RH11, RH13, RH14,
RA'08
ZHANG, S.L.--RB11
ZHANG, Y.--MF03
ZHAO, K.--RC10
ZHAO, S.--TD01
ZHAO, Z.Q.--TB03
ZHEN, M.--RB06
ZHENG, L.--RH01
ZHITNIKOV, R.A.--RF05
ZHU, X.--MG04, TA09
ZHUO, Q.--TA03
ZILBERG, S.--TF11
ZIMMERMANN, D.--FA08,
WG07, FA07
ZOBOV, N.--TC13
ZYRNICKI, W.--WH13

INFORMATION

ACCOMMODATIONS: The check-in for dormitory accommodations is located in Drackett Tower (F) on Curl Drive.

MAIL: Address your mail for delivery during the Symposium to: c/o MOLECULAR SPECTROSCOPY SYMPOSIUM, Department of Physics, The Ohio State University, 174 West 18th Avenue, Columbus, Ohio, 43210, U.S.A. FAX number - (614) 292-1948, Telephone number - (614) 292-2569.

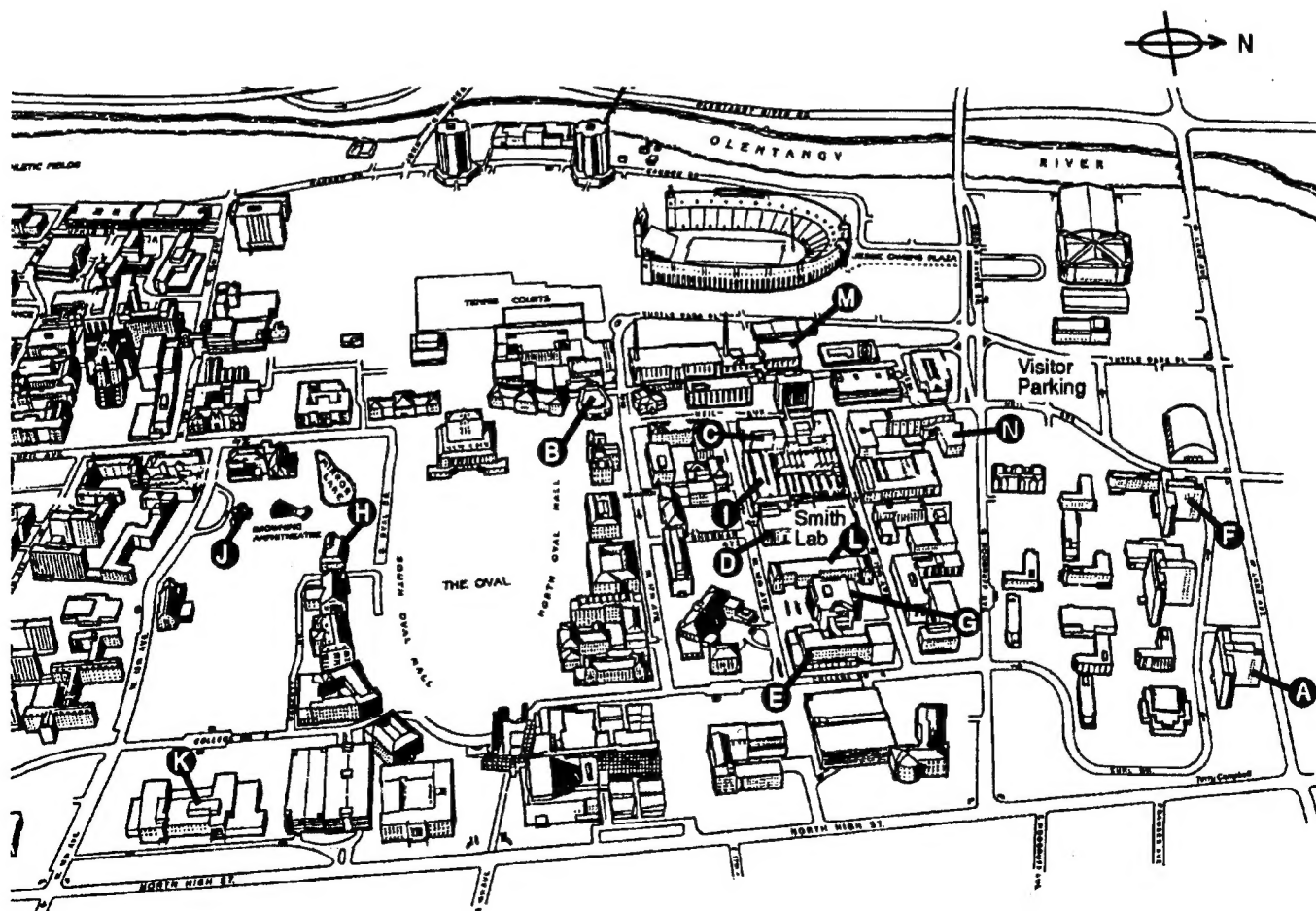
THE OHIO STATE UNIVERSITY

- A. Taylor Tower
- B. Independence Hall
- C. Post Office
- D. Smith Lab (Physics)
- E. Evans Laboratory (Chemistry)
- F. Drackett Tower (Check-In)
- G. New Chemistry -- Laser Spectroscopy Facility (Basement)
- H. Faculty Club
- I. Robinson Lab
- J. Kuhns Honors Hall
- K. Ohio Union
- L. McPherson Lab (Chemistry)
- M. Bookstore
- N. Hitchcock Hall

PARKING: Parking permits are available **only** from the check-in desk at Drackett Tower. These permits allow you to park in the Tuttle-Woodruff parking lot only. The permit must be displayed on the front windshield of your car. Please follow all traffic rules to avoid the issuance of tickets.

REGISTRATION: The Registration Desk will be located in Room 1036, Physics Laboratory. It will be kept open between 8:15 a.m. - 4:30 p.m., Monday through Friday. Those who have prepaid their registration and who are staying in the dorms will receive their registration packet at dormitory check-in. If you have prepaid your registration but are not staying at the dorms, pick up your packet at the Registration Desk. **NOTE: If the dates of your stay have changed since preregistering, please settle your account at the Drackett Tower front desk before you leave.**

SESSIONS: Overhead and slide (2"x2") projectors will be available for each session. If you are using slides, please give them to the projectionist at the beginning of the session. Sessions will be held in: Hitchcock Hall (N), Physics Lab (D), and McPherson Chemical Lab (L). Letters in parentheses correspond to the campus map below. Please note some rooms are different than in the past due to building renovations.



49TH OHIO STATE UNIVERSITY INTERNATIONAL SYMPOSIUM ON MOLECULAR SPECTROSCOPY
JUNE 13-17, 1994

	MONDAY JUNE 13TH 8:45AM	TUESDAY JUNE 14TH 8:30AM	WEDNESDAY JUNE 15TH 8:45AM	THURSDAY JUNE 16TH 8:30AM	FRIDAY JUNE 17TH 8:30AM
ROOM 131 HITCHCOCK HALL	MA. PLENARY SESSION RAO AWARDS COBLENTZ AWARD & LECTURE		WA. PLENARY SESSION		
ROOM 1153 SMITH LAB		TA. ELECTRONIC (SMALL)		RA. RYDBERG RA'. ELECTRONIC (SMALL)	FA. ELECTRONIC (SMALL)
ROOM 1009 SMITH LAB		TB. ULTRA-FAST		RB. RAMAN & INFRARED	FB. INFRARED
ROOM 1005 SMITH LAB		TC. MICROWAVE		RC. THEORY	FC. JET & BEAM
ROOM 100 MCPHERSON LAB		TD. INFRARED		RD. IONS & RADICALS	FD. THEORY FD'. POST DEADLINE

1:30PM

ROOM 1153 SMITH LAB	ME. INFRARED	TE. INFRARED TE'. IONS & RADICALS	WE. THEORY	RE. JET & BEAM	
ROOM 1009 SMITH LAB	MF. CONDENSED PHASE	TF. ELECTRONIC (LARGE)	WF. MICROWAVE	RF. MATRIX RF'. MICROWAVE	
ROOM 1005 SMITH LAB	MG. IONS & RADICALS	TG. MATRIX	WG. RYDBERG	RG. THEORY	
ROOM 100 MCPHERSON LAB	MH. ELECTRONIC (SMALL)	TH. RYDBERG	WH. ELECTRONIC (SMALL)	RH. INFRARED	